VOL. XXXI. APRIL, 1904. NO. 4.

AMERICAN

CHEMICAL JOURNAL

ON THE NATURE OF CONCENTRATED SOLUTIONS OF ELECTROLYTES—HYDRATES IN SOLUTION.

BY HARRY C. JONES AND FREDERICK H. GETMAN (CARNEGIE RESEARCH ASSISTANT).[1]

The present investigation is a continuation of the work that was begun in this laboratory by Jones and Chambers[2] in 1900. It had been observed by Jones and Ota[3] and by Jones and Knight[4] in connection with their work on the condition of double sulphates, chlorides, nitrates, cyanides, etc., in aqueous solution, that concentrated solutions of these substances frequently show abnormally great depression of the freezing-point of water. The first systematic study of this problem was made by Jones and Chambers.[5] They determined the molecular lowering produced by solutions of calcium chloride ranging in concentration from 0.102 to 0.612 normal. Similarly, they determined the molecular lowering produced by strontium chloride from 0.05 to 0.75 normal; by barium chloride from 0.0976 to 0.5858 normal; by magnesium chloride from 0.0508 to 0.6099 normal; by cadmium chloride from

[1] Dr. Getman was appointed Carnegie Research Assistant in October, 1903. The continuation of this investigation was, therefore, made possible by a grant from the Carnegie Institution.

[2] This JOURNAL, **23**, 89 (1900).

[3] *Ibid.*, **22**, 5 (1899).

[4] *Ibid.*, **22**, 110 (1899).

[5] *Loc. cit.*

0.214 to 1.072 normal; by calcium bromide from 0.04355 to 0.5226 normal; by strontium bromide from 0.052 to 0.621 normal; by barium bromide from 0.10 to 0.5 normal; by magnesium bromide from 0.0517 to 0.517 normal; by cadmium bromide from 0.22 to 0.88 normal.

With every salt studied, except cadmium chloride and bromide, the molecular lowering decreased with the concentration up to a certain point, and then increased as the concentration increased. In a word, there was a well-defined minimum in the curve expressing the relation between molecular lowering of the freezing-point and concentration of the solution.

The conductivities of these solutions increased regularly with the dilution, from the most concentrated to the most dilute solution, there being no indication of a minimum in any of the conductivity curves.

The work begun by Jones and Chambers was continued in this laboratory by Chambers and Frazer.[1]

They studied solutions of hydrochloric and phosphoric acids, of strontium and cadmium iodides, of sodium acetate, copper sulphate, and zinc chloride, in the same manner and approximately over the same range of concentration as had been done by Jones and Chambers. They found a more or less well-defined minimum in the freezing-point curve for every one of the above substances.

Somewhat more than two years ago we took up an extended investigation in this field, intending to study especially solutions of very great concentration. In all of the previous work the ordinary Beckmann thermometers, covering a range of 5° or 6°, had been used. It is obvious that these could not be employed for very concentrated solutions. We had two thermometers of the Beckmann type constructed, one having a range of 12° and graduated to fiftieths of a degree, the other having a range of 25° and graduated to twentieths of a degree. The latter was used for the most concentrated solutions, while the former was employed with solutions of lesser

[1] This JOURNAL, 23, 512 (1900).

concentration, but still too concentrated to admit of the use of an ordinary Beckmann thermometer.

When the first part of our investigation was well under way a paper along the same general line was published by W. Biltz.[1] It surprised us that he should have entered this field at the time named, since Jones and Chambers and Jones and Frazer had stated in both papers that this line of investigation, which had been taken up systematically for the first time in this laboratory, would be continued here and pushed forward as rapidly as possible.

Biltz worked with sodium, potassium, ammonium, caesium, rubidium, lithium, mercuric, cupric, zinc, manganous, nickel, cobalt, and ferrous chlorides; potassium, lithium, aluminium, and cupric bromides; potassium and lithium iodides; potassium fluoride, potassium cyanide, potassium sulphocyanate, and lithium nitrate.

All of the above substances showed well-marked minima in the freezing-point curves, except potassium, lithium, and rubidium chlorides; potassium and aluminium bromides; lithium iodide, potassium cyanide, and potassium sulphocyanate.

Since the work of W. Biltz did not extend to any very great concentration, and the data which we had already obtained showed that this was the interesting and really important field to study, we did not modify our plans in the least because of the work that W. Biltz had done.

We, however, thought it advisable to publish some of the data which we had obtained at that time,[2] to indicate again the line along which we were working, and to avoid any duplication of work in the future.

The first part of our investigation has recently been published in full.[3] The compounds studied were hydrochloric acid, lithium chloride, ammonium chloride, sodium chloride, potassium chloride, calcium chloride, strontium chloride, barium chloride, nitric acid, lithium nitrate, ammonium nitrate, sodium nitrate, potassium nitrate, sulphuric acid, am-

[1] Ztschr. phys. Chem., 40, 185 (1902).
[2] This JOURNAL, 27, 433 (1902).
[3] Ztschr. phys. Chem., 46, 244 (1903). Phys. Rev., 18, 146 (1904).

monium sulphate, sodium sulphate, potassium sulphate, sodium carbonate, potassium carbonate, phosphoric acid, primary potassium phosphate, sodium hydroxide, and potassium hydroxide.

The freezing-point, conductivity, and refractivity of a number of solutions of these substances were measured, and in some cases the boiling-points were also determined. A few of the more interesting results that were obtained in concentrated solutions are given below. Table I. is for hydrochloric acid.

m = concentration in gram-molecular normal.

s = observed depression of the freezing-point.

k = correction for change in concentration due to separation of ice.

Δ = corrected depression of the freezing-point.

$\frac{\Delta}{m}$ = molecular depression of the freezing-point.

Hydrochloric Acid (*see Fig. I.*).

m.	s.	k.	Δ.	$\frac{\Delta}{m}$.
1.0	4.140	0.018	4.122	4.122
1.5	6.720	0.087	6.633	4.422
2.0	10.218	0.281	9.937	4.969
2.5	13.510	0.055	13.455	5.382
3.0	18.100	0.004	18.096	6.030

The conductivity measurements are tabulated in the usual manner; v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte, and $\mu_v 0^\circ$ = the molecular conductivity at 0°—the temperature the nearest comparable with those at which the freezing-point measurements were made, at which $\mu\infty$ could be determined.

v.	$\mu_v 0^\circ$.	v.	$\mu_v 0^\circ$.
2.0	216.50	0.500	170.19
1.0	200.32	0.400	152.38
0.667	182.35	0.333	141.87

The value of $\mu\infty$ for hydrochloric acid at 0°, from the work of Jones and Douglas,[1] is 240.6. Knowing this value, we can

[1] This JOURNAL, 26, 434 (1901).

calculate the dissociation of each of the above solutions. The values are:

v.	Dissociation α. Per cent.	*v.*	Dissociation α. Per cent.
2.000	90.0	0.500	70.7
1.000	83.3	0.400	63.3
0.667	75.8	0.333	58.9

The most concentrated solution of hydrochloric acid that was studied was dissociated only about 59 per cent, and yet showed a molecular lowering of the freezing-point of 6.03.

If hydrochloric acid—a binary electrolyte—was completely dissociated it would give a molecular lowering of only $1.86 \times 2 = 3.72$. Being about 60 per cent dissociated, the molecular lowering would be calculated thus:

$$i - 1 = \alpha$$
$$\alpha + 1 = i$$

In this case $i = 1.60$.

But $$\frac{\text{mol. lowering}}{1.86} = i.$$

Molecular lowering $= 1.86 \times 1.60 = 2.97$.

The difference between, in round numbers, 3 and 6, is the magnitude of the apparent abnormality in the freezing-point lowering, as shown by a three-normal solution of hydrochloric acid.

Our theory to account for this and all similar phenomena is that in concentrated solutions there is combination between the solvent and dissolved substance, thus removing from the field of action, as far as freezing-point lowering is concerned, a part of the solvent, in reality, concentrating the solution by just so much.

We cannot calculate accurately the number of molecules of water in combination in any solution with 1 molecule or ion of the dissolved substance, unless we know the specific gravity and concentration of the solution, which would tell us just how much water was present in a liter of that solution. We propose to take up this side of the question a little later, and calculate for many of the solutions studied the exact number

of molecules of water combined with 1 molecule of the dissolved substance. However, from data already at hand, we can say that in a three-normal solution every molecule of hydrochloric acid, dissociated or undissociated, is combined with about 8 molecules of water.

Before leaving hydrochloric acid, it should be pointed out, that, while there is a minimum in the freezing-point curve at about 0.1 normal, the conductivity curve shows no sign of a minimum, in this or any other region that has been studied.

Turning to sulphuric acid, the following data were obtained :

Sulphuric Acid (*see Fig. I.*).

m.	*s.*	*k.*	Δ.	$\frac{\Delta}{m}$.
0.10	0.413	0.016	0.397	3.970
0.30	1.180	0.024	1.156	3.853
0.50	2.040	0.023	2.017	4.034
1.00	4.203	0.014	4.189	4.189
1.50	7.450	0.007	7.443	4.962
2.00	11.300	0.004	11.296	5.648
2.50	16.275		16.275	6.510

v.	$\mu_v 0°$.	*v.*	$\mu_v 0°$.
2.000	277.30	0.333	155.29
1.000	253.44	0.286	135.00
0.667	221.25	0.250	118.86
0.500	199.42	0.222	100.21
0.400	178.79	0.200	86.97

The dissociation of the above solutions of sulphuric acid at 0° can be readily calculated. Jones and Douglas[1] determined the value of $\mu\infty$ for sulphuric acid at zero, and found it to be 500. The dissociations of the above solutions of sulphuric acid are :

v.	*α.*	*v.*	*α.*
	Per cent.		Per cent.
2.000	55.46	0.333	31.06
1.000	50.69	0.286	27.00
0.667	44.25	0.250	23.77
0.500	39.88	0.222	20.04
0.400	35.76	0.200	17.39

[1] This JOURNAL, **26**, 428 (1901).

Take the twice normal solution of sulphuric acid ; it is dissociated only 17.4 per cent, and gives a molecular lowering of the freezing-point of water of 5.648. The molecular lowering would be calculated from the dissociation as follows, sulphuric acid being a ternary electrolyte :

$$\alpha = \frac{i-1}{2};$$

$$i = 1.348;$$

$$\frac{\text{Molecular lowering}}{1.86} = i = 1.348.$$

Molecular lowering $= 2.50$.

In a manner similar to that employed in the case of hydrochloric acid we can calculate approximately the number of molecules of water combined with 1 molecule of sulphuric acid in a twice-normal solution of the acid. We find it to be about 14 molecules.

There are two other substances that were studied in this earlier work, which should be briefly mentioned in this connection, on account of the very large lowering of the freezing-point of water produced by them. They are calcium chloride and strontium chloride.

Calcium Chloride (*see Fig. I.*).

m.	s.	k.	Δ.	$\frac{\Delta}{m}$.
0.05				4.85
0.10				4.98
0.20				4.96
0.30				5.02
0.40				5.16
0.50				5.26
1.00	6.350	0.005	6.345	6.345
1.50	11.300	0.004	11.296	7.531
2.00	17.875	0.008	17.867	8.934

v.	$\mu_v 0°$.	v.	$\mu_v 0°$.
1.000	71.16	0.500	53.98
0.667	62.14	0.400	44.79

Strontium Chloride (*see Fig. I.*).

m.	s.	k.	Δ.	$\frac{\Delta}{m}$.
0.05				5.16
0.10				4.88
0.20				4.87
0.30				4.90
0.40				4.95
0.50				5.09
1.00	6.010	0.010	6.000	6.000
1.5	10.725		10.725	7.150
2.0	16.425	0.003	16.422	8.211

v.	$\mu_v 0°$.	v.	$\mu_v 0°$.
2.000	84.27	0.667	63.01
1.000	74.57	0.500	55.26

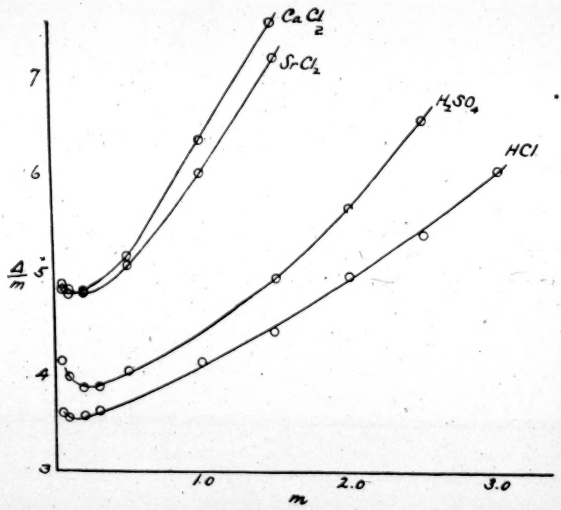


Fig. I.

The double-normal solutions of these chlorides are dissociated, probably, about 30 per cent. We shall determine this

accurately a little later. On this basis the molecular lowering produced by a twice-normal solution of calcium chloride would be 3.0, while the lowering actually found was 8.9. This, corrected for specific gravity, would show that each molecule of calcium chloride was combined with about 19 molecules of water in a double-normal solution. Each molecule of strontium chloride would be combined with 1 or 2 molecules less.

Of the compounds studied in this earlier work, all except sodium nitrate, potassium nitrate, the sulphates of sodium, potassium, and ammonium, and primary potassium phosphate show a minimum in the freezing-point curves, and from this minimum the molecular lowering increases with the concentration as well as with the dilution.

All of the twenty-two substances studied in this part of the investigation gave conductivity curves which are perfectly normal, showing no irregularities whatever in the region where the minimum of molecular depression manifests itself; the molecular conductivity increasing regularly with the dilution. The refractivity curves also show no irregularities at any point, being for the most part nearly straight lines.

The boiling-point curves obtained in this part of the work also show minima, analogous to the freezing-point curves. Since more accurate boiling-point determinations will be recorded later in this paper, a fuller discussion of this subject will appear further on.

The discussion of the meaning of these various curves will be reserved until later in this paper.

Second Part of This Investigation.

The above investigation was extended to fifteen compounds, and the prime object of this paper is to record the results obtained. These are: Manganese chloride, manganese sulphate, manganese nitrate, nickel chloride, nickel sulphate, nickel nitrate, cobalt chloride, cobalt sulphate, cobalt nitrate, cupric chloride, copper sulphate, cupric nitrate, aluminium chloride, aluminium sulphate, and aluminium nitrate.

In the tables given below the symbols have the following significance:

In "Freezing-point Measurements," m is the concentration in terms of gram-molecular normal, Δ the corrected lowering of the freezing-point, and $\frac{\Delta}{m}$ the molecular lowering.

In "Conductivity Measurements," v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte.

Under "Refractivity Measurements" m is the concentration in terms of gram-molecular normal, λ the reading on the Pulfrich refractometer, and n the index of refraction.

Manganese Salts.

The results with the manganese salts are recorded in Tables I. to IX., and the results are plotted in Figs. II. to IV.

Manganese Chloride,
$MnCl_2$—125.9.

Table I.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.053	0.255	4.81
0.106	0.508	4.79
0.133	0.639	4.80
0.266	1.259	4.73
0.400	2.004	5.01
0.532	2.790	5.24
0.796	4.247	5.34
0.902	4.825	5.36
1.061	5.965	5.62

Table II.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
18.87	88.67	1.88	65.16
9.43	81.81	1.26	57.32
7.51	79.85	0.94	51.44
3.76	73.49		

Table III.—Refractivity Measurements.

m.	λ.	n.
0.053	67° 7′	1.32656
0.106	66° 53′	1.32766
0.133	66° 45′	1.32829
0.266	66° 5′	1.33150
0.533	64° 50′	1.33768
0.796	63° 40′	1.34363
0.902	63° 14′	1.34588

Manganese Nitrate,

$Mn(NO_3)_2$—179.08.

Table IV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.035	0.090	2.56
0.18	0.410	2.25
0.35	0.841	2.40
0.53	1.297	2.44
0.87	2.184	2.51
1.05	2.748	2.61
2.10	6.310	3.05
2.80	9.315	3.33
3.50	12.690	3.63

Table V.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
28.6	49.18	0.95	33.35
5.56	44.33	0.47	29.10
2.85	41.79	0.36	24.49
1.89	39.60	0.29	21.95
1.15	36.80		

Table VI.—Refractivity Measurements.

m.	λ.	n.
0.035	67° 20′	1.32554
0.18	66° 55′	1.32751
0.35	66° 30′	1.32949
0.53	66° 4′	1.33142
0.87	65° 15′	1.33643
1.05	64° 50′	1.33768
2.10	62° 30′	1.34974
2.80	61° 5′	1.35734
3.50	59° 44′	1.36459

Manganese Sulphate,
$MnSO_4$—151.06.

Table VII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.08	0.194	2.43
0.16	0.354	2.21
0.25	0.510	2.04
0.33	0.676	2.04
0.41	0.792	1.94
0.82	1.556	1.90
0.98	1.898	1.93
1.31	2.701	2.06
1.64	3.668	2.23

Table VIII.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
12.5	52.78	1.22	26.29
6.25	44.48	1.02	23.70
4.00	38.35	0.76	19.50
3.03	35.65	0.61	16.20
2.50	34.25		

Table IX.—Refractivity Measurements.

m.	λ.	n.
0.08	66° 55′	1.32750
0.16	66° 28′	1.32965
0.25	66° 5′	1.33150
0.33	65° 39′	1.33362
0.41	65° 16′	1.33575
0.82	63° 19′	1.34545
0.98	62° 35′	1.34930
1.31	61° 13′	1.35661
1.64	59° 57′	1.36357

The chloride shows a minimum in the molecular lowering at about 0.2 normal; the minimum for the nitrate is at a slightly greater concentration, while the sulphate does not show the freezing-point minimum until a concentration of about 0.8 normal is reached. The positions of these minima are clearly seen in Fig. II. The molecular lowering of manganese chloride is about 5.6 at normal concentration, while the molecular lowering of manganese nitrate at 3.5 normal is only 3.6.

The molecular lowering produced by manganese sulphate at normal concentration is less than 2. Similar relations will appear when the salts of other heavy elements are compared, the sulphates in general showing much smaller lowerings of the freezing-point than the chlorides and nitrates.

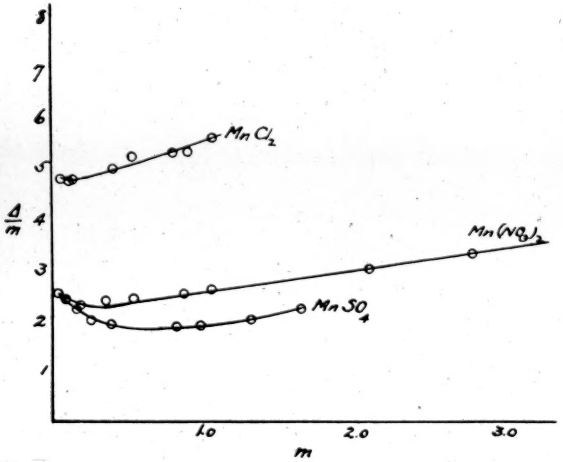


Fig. II.

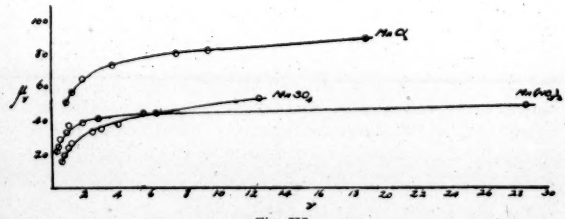


Fig. III.

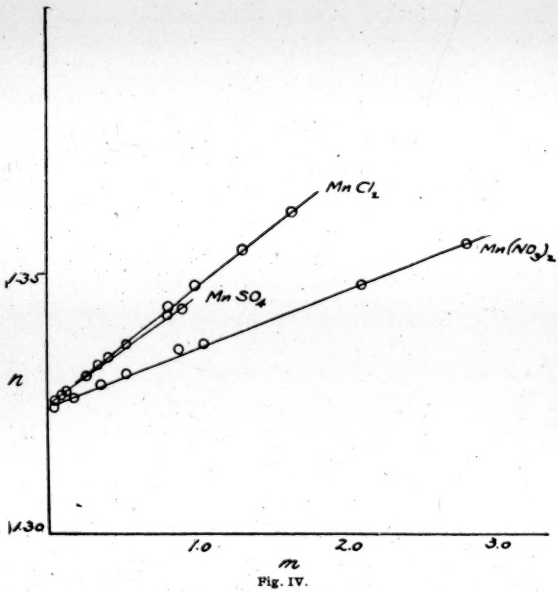


Fig. IV.

The molecular conductivities of all these salts increase regularly with the concentration, as can be seen in Tables II., V., and VIII., and in Fig. III. There is no sign of a minimum in the conductivity curves at any dilution used in this investigation. The refractivity data (Tables III., VI., and IX.) show that the index of refraction, for all three manganese salts, increases with the concentration. When these data are plotted as curves, the concentrations as abscissæ, and the indices of refraction as ordinates, the curves are very nearly straight lines. The complete absence of minima is therefore obvious.

Salts of Nickel.

The results with the salts of nickel are recorded in Tables

X. to XVIII., and the results are plotted in Figs. V. to VII.

Nickel Chloride,
$NiCl_2$—129.6.

Table X.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.037	0.205	5.54
0.074	0.380	5.11
0.149	0.768	5.15
0.223	1.170	5.25
0.297	1.585	5.34
0.372	2.032	5.46
0.446	2.458	5.51
0.521	2.945	5.65
0.743	4.547	6.12

Table XI.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
27.0	103.2	2.68	77.9
13.5	97.0	2.24	77.2
6.7	88.64	1.92	75.2
4.48	85.50	1.35	70.23
3.38	82.52		

Table XII.—Refractivity Measurements.

m.	λ.	n.
0.037	67° 5′	1.32672
0.074	66° 50′	1.32790
0.149	66° 22′	1.32965
0.223	65° 56′	1.33240
0.297	65° 26′	1.33485
0.372	65° 00	1.33684
0.446	64° 35′	1.33894
0.521	64° 10′	1.34106
0.743	63° 00	1.34710

Nickel Nitrate,

$Ni(NO_3)_2$—182.78.

Table XIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0761	0.377	4.95
0.1522	0.750	4.93
0.3044	1.527	5.01
0.6088	3.273	5.37
0.7610	4.306	5.66
1.0654	6.691	6.28
1.2176	8.006	6.58
1.5220	10.883	7.15

Table XIV.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
13.13	90.90	1.31	61.90
6.57	85.14	0.90	55.30
3.25	76.00	0.82	52.28
1.64	68.60	0.65	45.29

Table XV.—Refractivity Measurements.

m.	λ.	n.
0.0761	66° 51′	1.32782
0.1522	66° 25′	1.32989
0.3044	65° 33′	1.33378
0.6088	63° 50′	1.34277
0.7610	63° 05′	1.34667
1.0654	61° 32′	1.35463
1.2176	60° 50′	1.35870
1.5220	59° 24′	1.36653

Nickel Sulphate,

$NiSO_4$—154.76.

Table XVI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.048	0.130	2.70
0.097	0.227	2.34
0.145	0.320	2.21
0.290	0.550	1.90
0.386	0.720	1.87
0.483	0.874	1.81
0.579	1.023	1.77
0.869	1.532	1.76
0.965	1.724	1.79

Table XVII.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
20.83	54.6	2.07	31.16
10.31	47.1	1.73	29.56
6.89	44.8	1.15	25.08
3.45	37.67	1.03	23.40
2.59	35.92		

Table XVIII.—Refractivity Measurements.

m.	λ.	n.
0.048	67° 00′	1.32711
0.097	66° 40′	1.32869
0.145	66° 25′	1.32989
0.290	65° 30′	1.33436
0.386	64° 55′	1.33726
0.483	64° 25′	1.33978
0.579	63° 45′	1.34320
0.869	62° 25′	1.35018
0.965	61° 55′	1.35285

Nickel chloride shows a minimum in the molecular lowering of the freezing-point in the neighborhood of 0.5 normal. The nitrate of nickel shows the freezing-point minimum at about the same concentration. The sulphate of nickel, like the sulphate of manganese, does not show the freezing-point minimum until a much greater concentration is reached than that at which it appeared with the chloride and nitrate. The positions of the minima in the case of the three salts of nickel can be seen at once by referring to Fig. V. This also shows the actual values of the molecular lowerings produced by the three salts. The chloride gives a molecular lowering of 6.12 at 0.743 normal; the nitrate at this concentration giving a molecular lowering of only about 5.6. The most concentrated solution of the nitrate investigated—1.522 normal—gave, however, a molecular lowering as great as 7.15.

The molecular lowering of nickel sulphate, in addition to showing a minimum, presents another point of very special interest. The molecular lowering produced by nickel sulphate is very small, and in the most concentrated solutions studied is less than the constant for water. This means that in such solutions the nickel sulphate is polymerized, and to

an extent that more than overcomes any electrolytic dissociation that may have taken place. Consequently, the molecular lowering is less than would be produced by a completely undissociated, non-polymerized substance.

The molecular conductivities of all three of the nickel com-

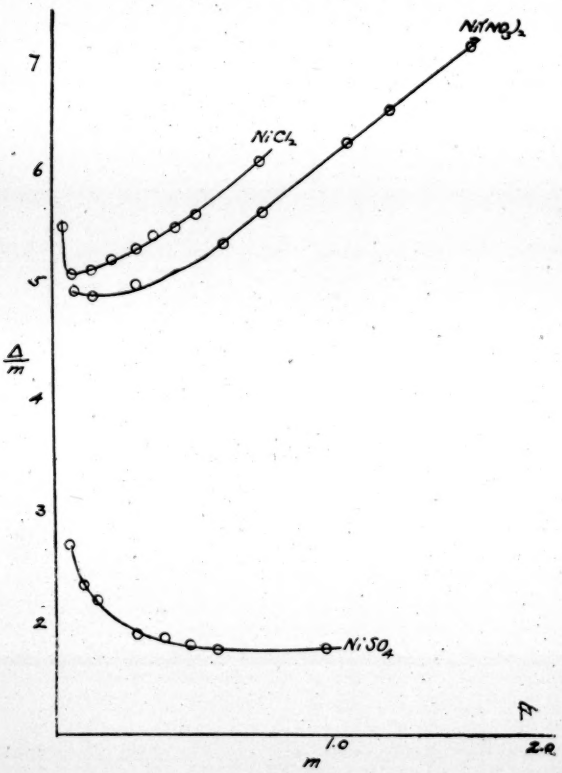


Fig. V.

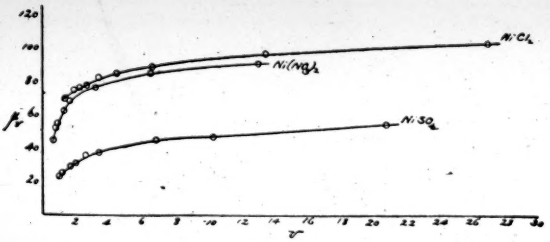


Fig. VI.

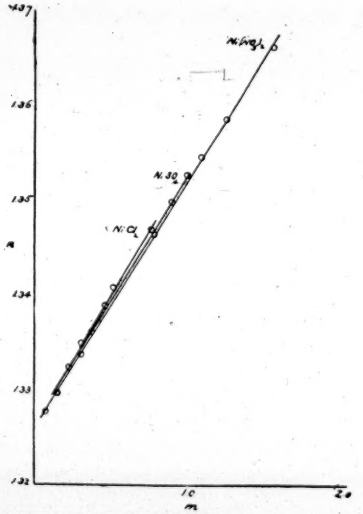


Fig. VII.

pounds increase regularly with the dilution, from the most concentrated to the most dilute solution that we employed. This is seen from the results in tables XI., XIV., and XVII., and is represented graphically in Fig. VI.

The refractivity data for the three salts of nickel are given in Tables XII, XV., and XVIII. The index of refraction in each case increases regularly with the dilution, and when index of refraction is plotted as one ordinate and concentration as the other, the resulting curve is practically a straight line for all three compounds.

Salts of Cobalt.

The data for the three compounds of cobalt that were studied are given in Tables XIX. to XXVII., and the results are plotted as curves, Figs. VIII. to X.

Cobalt Chloride,

$CoCl_2$—129.9.

Table XIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0639	0.325	5.09
0.1279	0.631	4.94
0.1918	0.946	4.93
0.3197	1.640	5.13
0.4475	2.427	5.43
0.5114	2.817	5.51
0.6393	3.658	5.72

Table XX.—Conductivity Measurements.

v.	μ_v.	v.	μ_v.
15.65	95.93	2.23	74.45
7.82	88.42	1.95	71.53
5.21	86.36	1.57	67.94
3.12	79.50		

Table XXI.—Refractivity Measurements.

m.	λ.	n.
0.0639	66° 53′	1.32735
0.1279	63° 27′	1.33005
0.1918	66° 5′	1.33151
0.3197	65° 20′	1.33518
0.4475	64° 37′	1.33910
0.5114	64° 15′	1.34064
0.6393	63° 36′	1.34415

Cobalt Nitrate,

$Co(NO_3)_2$—183.08.

Table XXII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0747	0.353	4.72
0.1495	0.685	4.58
0.2989	1.388	4.65
0.4484	2.198	4.87
0.7473	3.935	5.28
1.0462	6.025	5.76
1.3451	8.418	6.26
1.4945	9.811	6.55

Table XXIII.—Conductivity Measurements.

v.	μ_v	v.	μ_v.
13.39	87.68	1.35	62.43
6.69	81.80	0.95	54.60
3.35	75.00	0.74	48.17
2.23	69.46	0.67	45.47

Table XXIV.—Refractivity Measurements.

m.	λ.	n.
0.0747	66° 50′	1.32790
0.1495	66° 25′	1.32989
0.2989	65° 35′	1.33395
0.4484	64° 48′	1.33837
0.7473	63° 18′	1.34606
1.0462	61° 55′	1.35285
1.3451	60° 30′	1.36053
1.4945	59° 52′	1.36347

Cobalt Sulphate,

$CoSO_4$—155.06.

Table XXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0567	0.143	2.52
0.1133	0.245	2.16
0.2267	0.435	1.92
0.3399	0.625	1.84
0.6799	1.187	1.75
0.9066	1.614	1.77
1.1333	2.073	1.82

Table XXVI.—Conductivity Measurements.

$v.$	$\mu_v.$	$v.$	$\mu_v.$
17.64	57.49	1.47	30.67
8.82	48.56	1.10	27.16
4.41	42.06	0.89	23.15
2.94	38.07		

Table XXVII.—Refractivity Measurements.

$m.$	$\lambda.$	$n.$
0.0567	66° 55′	1.32751
0.1133	66° 35′	1.32909
0.2267	65° 57′	1.33248
0.3399	65° 20′	1.33518
0.6799	63° 37′	1.34423
0.9066	62° 30′	1.34974
1.1199	62° 00′	1.35240
1.1333	61° 30′	1.35508

The chloride of cobalt shows a minimum in the molecular lowering of the freezing-point at a concentration of about 0.2 normal. The nitrate shows the minimum at about the same concentration, while the sulphate does not show a minimum in the molecular lowering of the freezing-point until a concentration of 0.7 to 0.8 normal is reached.

It is also worth noting that the chloride of cobalt, like the chloride of nickel and the chloride of manganese, gives a greater lowering of the freezing-point of water, at the same concentration, than the corresponding nitrate.

The above results are shown graphically in Fig. VIII. The chloride gives a molecular lowering of 5.72 at 0.6393 normal, while the nitrate at this concentration produces a molecular lowering of about 5.0. The most concentrated solution of the nitrate, 1.4948 normal, showed a molecular lowering of 6.55.

The molecular lowering produced by cobalt sulphate, like that of nickel sulphate, is very small indeed. In the most concentrated solutions studied it is less than the constant for water. This is to be interpreted in the same manner as in the case of the nickel salt. There is undoubtedly polymerization here, to such an extent as to more than overcome the effect of electrolytic dissociation.

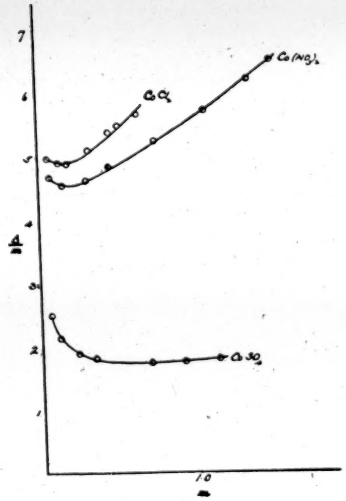


Fig. VIII.

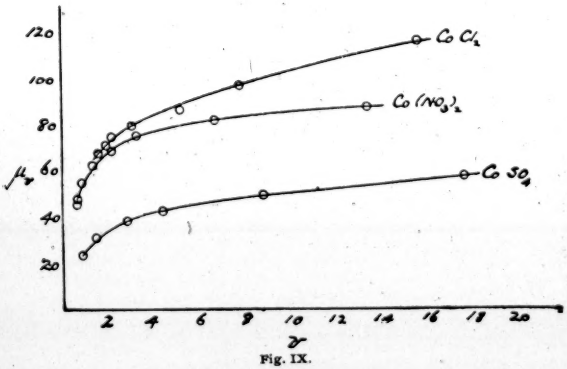


Fig. IX.

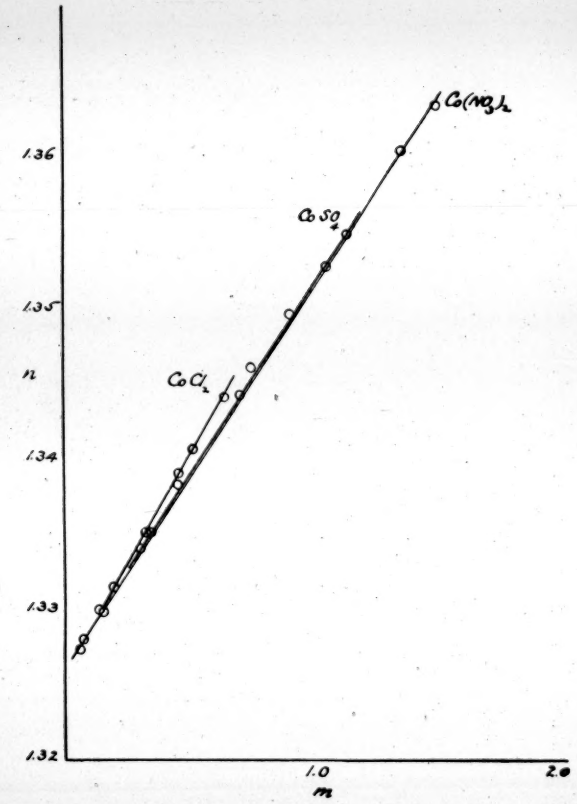


Fig. X.

The conductivities of the three salts of cobalt are given in Tables XX., XXIII., and XXVI., and are plotted in Fig. IX. The curves are all perfectly regular. It should be noted that the conductivity results resemble the freezing-

point results in this, that the chloride has greater conductivity than the nitrate for comparable concentrations, and the nitrate in turn has greater conductivity than the sulphate. This applies also to the salts of nickel and of manganese. The above results are what would be expected, since the chloride and nitrate are ternary electrolytes, while the sulphate is a binary electrolyte.

The refractivities of the three salts of cobalt are given in Tables XXI., XXIV., and XXVII., and plotted against concentration in Fig. X. The curves are perfectly regular and are nearly straight lines.

Copper Salts.

The results obtained with the three salts of copper are given in Tables XXVIII. to XXXIV.

Cupric Chloride,

$CuCl_2$—134.5.

Table XXVIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.065	0.331	5.09
0.1301	0.639	4.91
0.2602	1.273	4.89
0.5204	2.711	5.29
0.7806	4.413	5.65
1.3010	8.395	6.45
1.5612	10.383	6.65
1.8210	12.960	7.12
2.0816	15.480	7.43
2.6020	20.820	8.00

Table XXIX.—Conductivity Measurements.

v.	μ_v.	Dissociation. Per cent.
15.3	94.42	58.5
7.64	88.06	53.4
3.84	78.38	47.5
1.92	67.68	41.0
1.28	59.30	35.9
0.76	48.22	29.2
0.64	39.32	23.8
0.55	35.02	21.2
0.48	30.81	18.9
0.38	22.58	13.7

$\mu\infty\ 0°$[1] 165

[1] For the determination of this and subsequent values of $\mu\infty$ see page 351.

Table XXX.—Refractivity Measurements.

m.	λ.	n.
0.065	66° 53′	1.32735
0.1301	66° 25′	1.32989
0.2602	65° 39′	1.33428
0.5204	64° 10′	1.34106
0.7806	62° 45′	1.34842
1.3010	60° 12′	1.36163
1.5612	58° 55′	1.36934
1.8210	57° 43′	1.37579
2.0816	56° 40′	1.38222
2.6020	54° 30′	1.39491

Cupric Nitrate,
$Cu(NO_3)_2$—187.68.

Table XXXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0591	0.326	5.52
0.1182	0.595	5.03
0.2363	1.210	5.12
0.4726	2.544	5.39
0.9452	5.903	6.26
1.1815	7.799	6.60
1.6541	12.650	7.07
1.8904	15.490	8.20
2.3630	21.890	9.26

Table XXXII.—Conductivity Measurements.

v.	μ_v.	Dissociation. Per cent.
16.9	99.36	64.1
8.46	93.05	60.0
4.23	82.97	52.3
2.12	73.16	47.2
1.05	58.45	37.7
0.84	52.34	33.3
0.60	40.70	26.3
0.52	35.84	23.1
0.42	26.70	17.2

$\mu\infty 0° \quad 155$

Table XXXIII.—Refractivity Measurements.

m.	λ.	*n.*
0.0591	66° 55′	1.32751
0.1182	66° 30′	1.32949
0.2363	65° 51′	1.33199
0.4726	64° 25′	1.32979
0.9452	61° 50′	1.35329
1.1815	60° 40′	1.35961

Cupric Sulphate,
$CuSO_4$—159.66.

Table XXXIV.

m.	Δ.	$\frac{\Delta}{m}$.
0.072	0.172	2.33
0.144	0.312	2.16
0.476[1]	0.714	1.50
0.595[1]	0.866	1.45
0.890[1]	1.275	1.43
1.190[1]	1.740	1.46

The results are plotted as curves in Figs. XI. to XIII. The minimum in the molecular lowering of the freezing-point occurs, for copper chloride, at about 0.2 normal, for copper nitrate at about 0.1 normal, while for copper sulphate an apparent minimum occurs at about 0.9 normal, but this is not well defined.

There are a number of points of interest in connection with the freezing-point data and curves (Fig. XI.) of the copper salts. In the first place one is impressed with the great magnitude of the molecular lowering in concentrated solution, of copper chloride and copper nitrate. The chloride, at a concentration of 2.6 normal, shows a molecular lowering of 8.0; while the nitrate, at a concentration of 2.363 normal, gives a molecular lowering of 9.26. This is the largest molecular lowering produced by any substance thus far recorded in this paper. It might, also, be noted that copper nitrate gives a larger lowering, for comparable concentration, than copper chloride, which is the opposite of what was observed with manganese, nickel, and cobalt.

The molecular lowering of the freezing-point of water pro-

[1] Measurements by Chambers and Frazer. This JOURNAL, 23, 512.

duced by copper sulphate is smaller than that produced by any other compound which has come within the scope of our work. It falls to 1.43 at a concentration of 0.89 normal, and then apparently increases slightly with increase in concentration. Since this value is so far below the constant for water, 1.86, we must conclude that there is considerable polymerization in the more concentrated solutions of copper sulphate.

The conductivities of copper chloride and copper nitrate (Tables XXIX. and XXXII., and Fig. XII.) increase regularly with the dilution.

The conductivity of copper nitrate, like the freezing-point lowering is, for comparable concentrations, greater than that

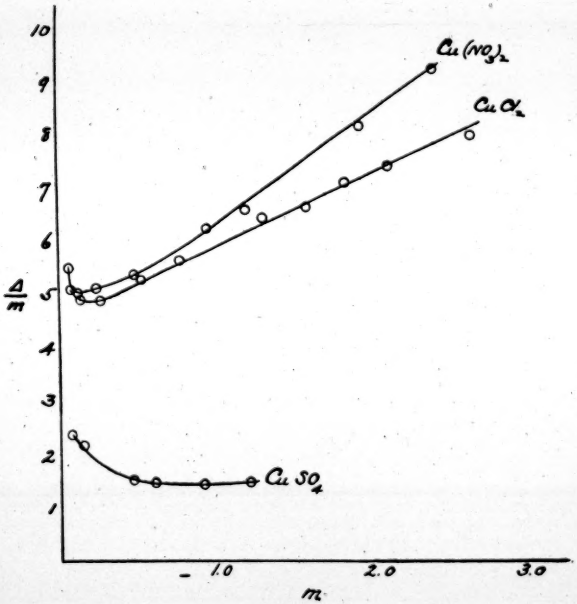


Fig. XI.

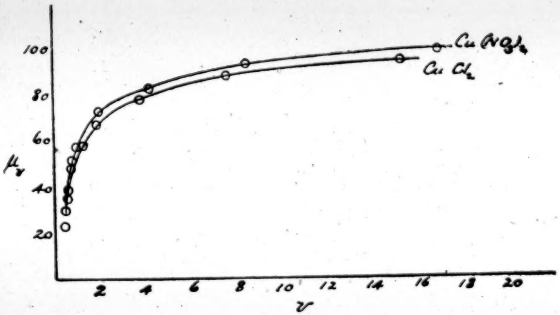


Fig. XII.

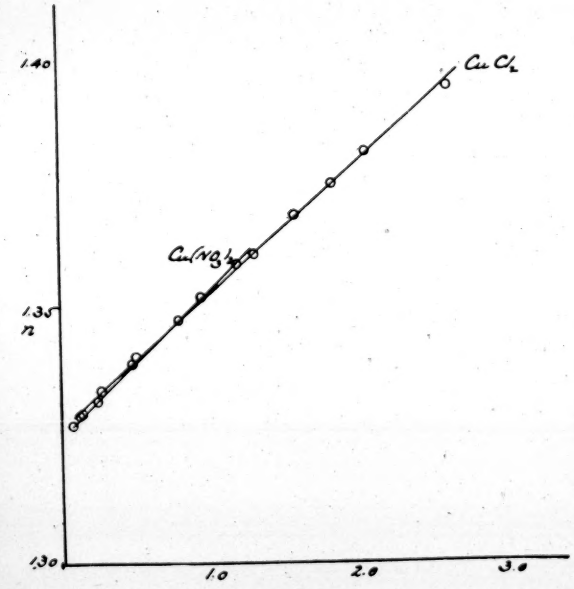


Fig. XIII.

of the chloride. The opposite was observed with the chlorides and nitrates of manganese, nickel, and cobalt. Since it was impossible to prepare a very concentrated solution of copper sulphate, the conductivities of this substance were not measured.

The refractivities of cupric chloride and nitrate are given in Tables XXX. and XXXIII., and the results are plotted in Fig. XIII. The refractivities of copper sulphate were not measured, since concentrated solutions could not be prepared. The refractivity curves of the chloride and nitrate are practically straight lines, showing no irregularity.

Salts of Aluminium.

The results for the three salts of aluminium are given in Tables XXXV. to XLVI. They are plotted in curves, Figs. XIV. to XVI. The minimum in the molecular lowering for aluminium chloride is at about 0.1 normal, and at about the same concentration for aluminium nitrate. No minimum was observed in the case of aluminium sulphate, probably because a solution of sufficient concentration could not be prepared.

Aluminium Chloride,
$AlCl_3$—133.46.

Table XXXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.046	0.276	6.04
0.076	0.446	5.85
0.102	0.578	5.68
0.200	1.148	5.74
0.299	1.840	6.15
0.398	2.596	6.52
0.531	3.830	7.21
0.657	5.120	7.79
0.876	7.970	9.09
1.195	13.610	11.40
1.434	19.518	13.60
1.593	23.870	14.98
2.124[1]	45.000	21.18

[1] This solution was frozen by means of a mixture of solid carbon dioxide and alcohol, and the freezing temperature measured by an alcohol thermometer.

Table XXXVI.—Conductivity Measurements.

v.	μ_v.	Dissociation. Per cent.
18.80	124.6	73.3
4.70	104.6	59.8
2.35	88.64	52.1
1.45	71.7	42.2
0.94	59.3	34.9
0.67	43.1	25.3

$\mu_{\infty 0^\circ} = 170$

Table XXXVII.—Refractivity Measurements.

m.	λ.	n.
0.2124	65° 43′	1.33297
0.4248	64° 15′	1.34064
0.6372	62° 53′	1.34736
1.062	60° 20′	1.36145
1.0487	57° 54′	1.37493
2.124	54° 35′	1.39441

Table XXXVIII.—Specific Gravity Measurements.

m.	W_S.	W_{AlCl_3}.	W_{H_2O}.	Correction. Per cent.
0.2124	25.5593	0.7087	24.8506	0.60
0.4248	26.1216	1.4173	24.7043	1.18
0.6372	26.6408	2.1260	24.5142	1.94
1.0620	27.6952	3.5430	24.1522	3.39
1.4868	25.6581	4.9600	23.6981	5.21
2.1240	30.0789	7.0870	22.9190	8.32

Aluminium Nitrate,
$Al(NO_3)_3$—213.23.

Table XXXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0533	0.333	6.25
0.1066	0.652	6.12
0.2132	1.410	6.57
0.3198	2.290	7.15
0.5330	4.260	8.00
0.7462	6.760	9.06
0.8528	8.190	9.60
1.066	11.790	11.06

Table XL.—Conductivity Measurements.

v.	μ_v.	Dissociation. Per cent.
18.76	137.85	76.6
9.38	122.00	67.8
4.69	111.89	62.1
3.13	101.60	56.4
1.88	86.10	47.8
1.34	73.27	40.7
1.17	65.98	36.6
0.94	55.21	30.6

$\mu\infty\, 0^\circ = 180$

Table XLI.—Refractivity Measurements.

m.	λ.	n.
0.0533	66° 52′	1.32727
0.1066	66° 30′	1.32949
0.2132	65° 40′	1.33354
0.3198	64° 54′	1.33726
0.5330	63° 25′	1.34493
0.7462	62° 00′	1.35240
0.8528	61° 10′	1.35688
1.066	60° 5′	1.36283

Table XLII.—Specific Gravity Measurements.

m.	W_S.	$W_{Al(NO_3)_3}$.	W_{H_2O}.	Correction. Per cent.
0.0533	25.1615	0.2840	24.8775	0.49
0.1066	25.3858	0.5682	24.8176	0.73
0.2132	25.8260	1.1362	24.6898	1.24
0.3198	26.2487	1.7045	24.5442	1.82
0.5330	27.1053	2.8400	24.2653	2.94
0.7462	27.9300	3.9760	23.9540	4.18
0.8528	28.3283	4.5460	23.7823	4.87
1.0660	29.1080	5.6820	23.4260	6.30

Aluminium Sulphate,

$Al_2(SO_4)_3$—342.43.

Table XLIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0736	0.260	3.46
0.1841	0.683	3.71
0.2946	1.138	3.86
0.3682	1.521	4.13

Table XLIV.—Conductivity Measurements.

v.	μ_v.
13.58	80.62
5.43	62.41
3.39	50.84
2.71	44.89

Table XLV.—Refractivity Measurements.

m.	λ.	n.
0.0736	66° 13′	1.33086
0.1841	64° 40′	1.33852
0.2946	63° 16′	1.34588
0.3682	62° 25′	1.35018

Table XLVI.—Specific Gravity Measurements.

m.	W_S.	$W_{Al_2(SO_4)_3}$.	W_{H_2O}.	Correction. Per cent.
0.0736	25.5612	0.6300	24.9312	0.28
0.1841	26.4130	1.5757	24.8373	0.65
0 2946	27.3215	2.5200	24.8015	0.79
0.3682	27.9238	3.1500	24.7738	0.90

In examining the freezing-point data for aluminium chloride and nitrate, one is especially impressed with the enormous magnitude of the molecular lowering produced by these substances, aluminium chloride showing an apparent molecular lowering of 21.18 at 2.124 normal. Aluminium nitrate shows even a greater molecular lowering than the chloride for the concentrations at which it could be studied, as can be seen at once from the continuous curves in Fig. XIV. The molecular lowering shown by the most concentrated solution of aluminium chloride is nearly double that found for any other substance which we have studied. The significance of these facts will be taken up in the general discussion of the results. The large lowerings shown by aluminium chloride and nitrate in dilute solutions are doubtless due, in part, to hydrolysis.

The molecular conductivities of the aluminium compounds increase regularly with the dilution, as can be seen in Tables XXXVI., XL., and XLIV., and in Fig. XV. The nitrate has greater conductivity than the chloride, which is analogous to the freezing-point results.

The refractivities of the three compounds of aluminium

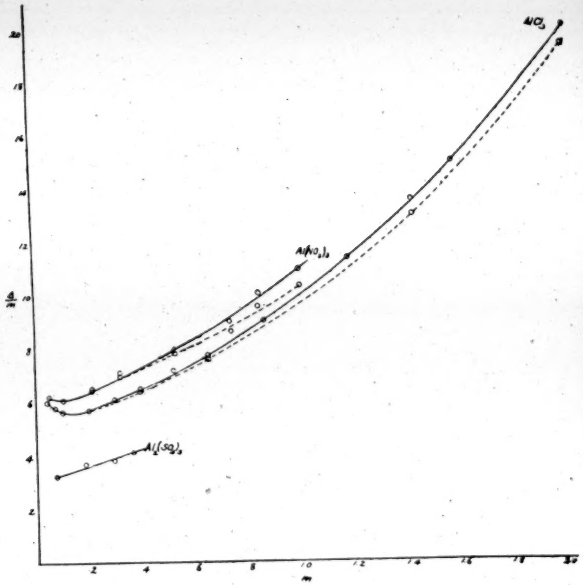


Fig. XIV.

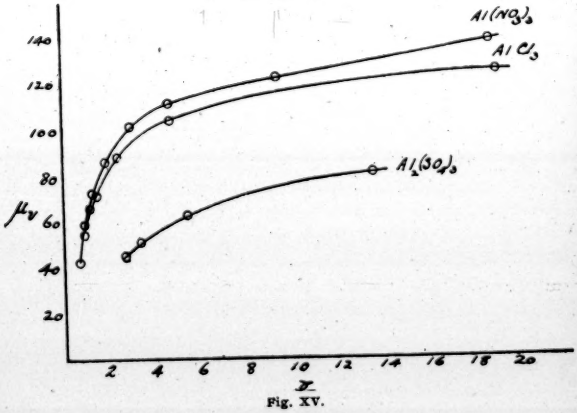


Fig. XV.

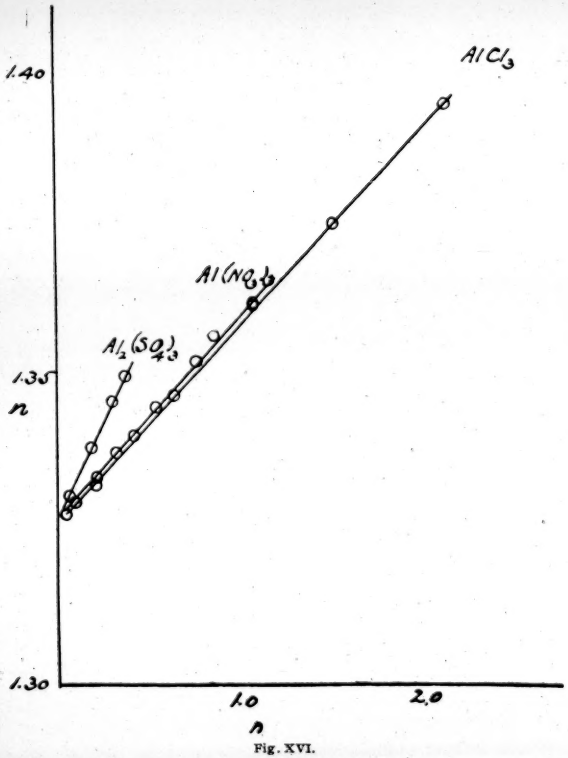


Fig. XVI.

(Table XXXVII., XLI., XLIV., and Fig. XVI.) are perfectly regular, always increasing with the concentration.

Specific gravity measurements were made and recorded with the three salts of aluminium. m is the concentration of the solution in terms of gram-molecular weight of the salt in a liter of the solution; W_S is the weight of 25 cc. of solution;

W_{AlCl_3} is the weight of aluminium chloride in 25 cc. of the the solution; W_{H_2O} is the weight of water in 25 cc. of the solution, and "Correction" is the percentage difference between the weight of water in 1 liter of the solution and 1,000 grams of water. In the more concentrated solutions this correction term becomes quite large—the amount of water in a liter of such solutions being much less than 1,000 grams.

In order that we should be able to calculate the amount of water combined with 1 molecule of the salt, as will be done later in this paper, this correction must be applied to the apparent molecular lowerings, giving the true molecular lowerings, which are the quantities that are nearly comparable with one another at all concentrations, and which can be compared directly with the freezing-point constant of water—1.86.

These corrections have already been applied to aluminium chloride and nitrate, and will be applied in a later paper to many other substances already studied, and to those that we are about to take up. The corrected results for the two compounds of aluminium are shown in the dotted curves, Fig. XIV. These are the true molecular lowerings produced by these substances, referred in every case to 1,000 grams of the solvent. The difference between the true and the observed lowerings becomes greater, of course, as the concentration increases. Reference will be made again to these results under the general discussion.

Determination of Rise in Boiling-points.

The rise in the boiling-point of water produced by a few compounds has been measured, using the Jones[1] apparatus, and the results are recorded in Tables XLVII. to LI.

In all of these determinations two pieces of apparatus were used, the one containing the pure solvent and the other the solution. They were both kept boiling simultaneously, and thus correction for barometric changes was avoided.

We have not yet had time to extend these measurements to a large number of substances. Although the task seems to be somewhat difficult, we hope to apply the boiling-point

[1] This JOURNAL, 19, 581 (1897).

Potassium Iodide (166.0) in Ethyl Alcohol.

Table XLVII.—Boiling-point Measurements.

First Series.

m.	f.	$\frac{f}{m}$.
0.052	0.080	1.54
0.061	0.090	1.47
0.073	0.106	1.45
0.088	0.125	1.42
0.125	0.175	1.40
0.174	0.250	1.43
0.237	0.343	1.45
0.250	0.355	1.42
0.266	0.373	1.40
0.286	0.407	1.42
0.296	0.420	1.42
0.317	0.450	1.42
0.337	0.479	1.42

Second Series.

0.045	0.070	1.55
0.060	0.090	1.50
0.071	0.105	1.48
0.095	0.140	1.47
0.102	0.150	1.47
0.112	0.165	1.47
0.145	0.213	1.47
0.373	0.530	1.42

Third Series.

0.021	0.032	1.54
0.032	0.050	1.56
0.045	0.070	1.55

Sodium Iodide (149.9) in Ethyl Alcohol.

Table XLVIII.

First Series.

m.	f.	$\frac{f}{m}$.
0.031	0.060	1.94
0.063	0.120	1.91
0.108	0.185	1.71
0.179	0.290	1.62
0.227	0.370	1.62
0.306	0.500	1.63
0.415	0.669	1.61
0.461	0.730	1.58

Second Series.

m.	f.	$\frac{f}{m}$.
0.042	0.080	1.90
0.092	0.150	1.74
0.123	0.205	1.67
0.139	0.225	1.62
0.601	0.925	1.54
0.875	1.440	1.64
1.344	2.470	1.83
1.661	3.300	1.99

Third Series.

0.022	0.045	2.05
0.041	0.078	1.90
0.076	0.125	1.64
0.140	0.225	1.61
0.230	0.360	1.56
0.307	0.480	1.56

Cadmium Iodide (366.1) in Ethyl Alcohol.

Table XLIX.

First Series.

m.	f.	$\frac{f}{m}$.
0.069	0.080	1.16
0.122	0.142	1.16
0.190	0.225	1.18
0.243	0.305	1.26
0.327	0.420	1.28
0.478	0.610	1.28
0.786	1.060	1.34
0.822	1.150	1.40
1.174	1.600	1.36
1.340	1.860	1.39
1.488	2.100	1.41
1.674	2.360	1.41
1.829	2.580	1.41

Second Series.

0.042	0.052	1.24
0.135	0.162	1.20
0.169	0.207	1.22
0.220	0.272	1.24
0.252	0.316	1.25
0.312	0.392	1.26
0.471	0.597	1.27
0.529	0.680	1.29

Third Series.

m.	*f*.	$\frac{f}{m}$.
0.012	0.018	1.50
0.041	0.050	1.22
0.058	0.068	1.17
0.089	0.110	1.23
0.119	0.142	1.19
0.156	0.188	1.21

Ammonium Iodide (144.94) in Ethyl Alcohol.

Table L.

First Series.

m.	*f*.	$\frac{f}{m}$.
0.017	0.030	1.76
0.056	0.090	1.60
0.134	0.200	1.49
0.178	0.265	1.49
0.231	0.350	1.52
0.277	0.435	1.57

Second Series.

0.019	0.032	1.68
0.031	0.051	1.64
0.077	0.120	1.56
0.124	0.190	1.53
0.150	0.222	1.47
0.185	0.277	1.50

Sodium Bromide (103.0) in Ethyl Alcohol.

Table LI.

First Series.

m.	*f*.	$\frac{f}{m}$.
0.103	0.140	1.36
0.135	0.185	1.36
0.156	0.210	1.34
0.224	0.290	1.29
0.267	0.335	1.25
0.331	0.395	1.19
0.363	0.440	1.21

Second Series.

m.	f.	$\frac{f}{m}$.
0.014	0.025	1.78
0.030	0.050	1.67
0.054	0.080	1.48
0.065	0.095	1.46
0.098	0.137	1.40
0.136	0.185	1.36
0.237	0.305	1.28
0.318	0.391	1.23

Third Series.

0.019	0.033	1.74
0.055	0.081	1.47

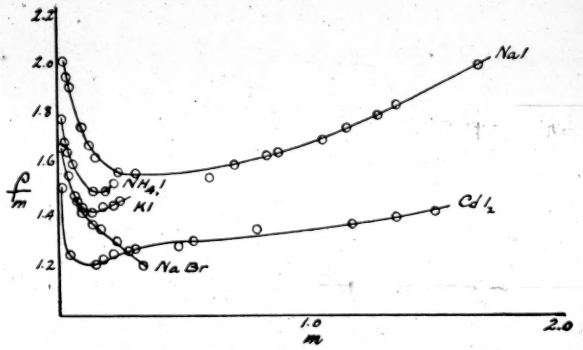


Fig. XVII.

method to a much larger number of the compounds, which have yielded such interesting results when the freezing-point method was applied to them.

Four of the five compounds studied by the boiling-point method show a well-defined minimum in the molecular rise of the boiling-point. Sodium bromide does not show such a minimum. The minimum in the case of rise in boiling-point is generally at a greater concentration than the freezing-point minimum for the same substances. This is exactly what

would be expected if the theory of hydrates in concentrated solutions, to account for these minima and the great freezing-point lowerings in concentrated solutions, is true. *These hydrates would be less stable at the higher temperatures*, and a greater concentration would, therefore, have to be reached before the effect of hydrate formation would so far overcome the influence of electrolytic dissociation as to cause the curve to pass through a minimum. This will, however, be referred to again.

General Discussion of the Results.

We have already studied in this laboratory from the above standpoint forty-nine compounds. Jones and Chambers[1] worked with ten salts. Chambers and Frazer[2] studied five salts and two acids. In our first paper[3] we described our work with twenty-three compounds, including seventeen salts, four acids, and two bases. Six of these substances, however, were the same as those used by Jones and Chambers, and Chambers and Frazer—more concentrated solutions being studied with the thermometers of wider range. In this paper we have given the results obtained for fifteen salts.

Of these forty-nine compounds forty-three are salts, four are acids, and two are bases. All of these substances show a minimum in the molecular lowering of the freezing-point except the following: Jones and Chambers found two exceptions, cadmium chloride and bromide. Chambers and Frazer failed to find more than one exception. Of those substances discussed in our first paper only sodium, potassium, and ammonium nitrates, sodium, potassium, and ammonium sulphates, and primary potassium phosphate failed to show a minimum in the freezing-point curve. Of the fifteen substances discussed in this paper, only aluminium sulphate fails to show any sign of a minimum, and, as is seen from the curve, Fig. XIV., this is because the proper dilution was not used. The minimum in the cases of nickel and cobalt sulphates is not very pronounced, but undoubtedly exists.

[1] This JOURNAL, 23, 89 (1900).
[2] *Ibid.*, 23, 512 (1900).
[3] Ztschr. phys. Chem., 46, 244 (1903). Phys. Rev., 18, 146 (1904).

Of the forty-nine compounds that have been studied in this laboratory only nine failed to show a minimum in the freezing-point curve. Some of these nine substances, however, showed abnormally great freezing-point lowerings in concentrated solutions, the normal freezing-point lowering of each being calculated from the conductivity.

Nearly every one of the forty-nine substances which we have studied, whether it does or does not show a freezing-point minimum, gives abnormally great depressions of the freezing-point of water in concentrated solutions, except two or three sulphates which are obviously polymerized in such solutions since the molecular lowerings are less than the constant for water. Some compounds show this phenomenon to a much greater extent than others, but they show it.

Explanation of the Above Fact.

The suggestion was made by Jones and Chambers[1] four years ago, to account for their results, that possibly the compounds, such as they had studied, combined with water in the more concentrated solutions. This suggestion was put forward purely tentatively, since it was the only apparent explanation of their results. They pointed out, however, as evidence in favor of this suggestion, that the chlorides and bromides of the alkaline earths, the substances with which they worked, were generally very hygroscopic substances when dehydrated, combining readily with water. With this idea in mind, Chambers and Frazer,[2] at the suggestion of Jones, with whom their work was done, selected those substances that are particularly hygroscopic, and found in every case, with the exception of copper sulphate, that the lowering in concentrated solutions was abnormally great.

Relation Between Water of Crystallization and Freezing-point Lowering.

We then took up the subject from a broader standpoint, determining to study all classes of substances with respect to this property. We find that while all substances except cer-

[1] This JOURNAL, **23**, 89 (1900).
[2] *Ibid.*, **23**, 512 (1900).

tain polymerized sulphates ($CuSO_4$, $NiSO_4$, $CoSO_4$) give abnormally great lowerings in concentrated solutions, the magnitude of this lowering varies greatly from one substance to another, and in general *those substances which crystallize out of solution with the largest number of molecules of water of crystallization, give the greatest molecular lowerings of the freezing-point of water in concentrated solution.* To take examples from our first paper, of all the chlorides studied in this part of our work, only calcium and strontium chlorides crystallize with six molecules of water. Barium chloride crystallizes with two molecules. Lithium chloride crystallizes below zero with two molecules of water of crystallization, while the alkali chlorides separate from solution with no water of crystallization. An examination of Fig. III., in our earlier paper,[1] will show that the curve for lithium chloride falls between those for the alkalies and the alkaline earths, and that the lowerings produced by calcium and strontium chlorides are very much greater than those produced by the alkali chlorides.

If we include also the work of Jones and Chambers,[2] which, however, did not extend to any very great concentration, we find that magnesium chloride, which, like calcium and strontium chlorides, has 6 molecules of water of crystallization, gives freezing-point depressions of the same order of magnitude as calcium and strontium chlorides; indeed, slightly larger depressions. Cadmium chloride, on the other hand, crystallizes with only 2 molecules of water and shows much less depression of the freezing-point.

The work of Jones and Chambers[3] shows that exactly the same relations obtain for the bromides of barium, strontium, calcium, and magnesium, as we have just seen to hold for the chlorides. Barium bromide crystallizes with 2 molecules of water, and gives the smallest lowering; strontium, calcium, and magnesium bromides each crystallize with 6 molecules of water of crystallization, and stand in the same order with re-

[1] Ztschr. phys. Chem., **46**, 281 (1903). Phys. Rev., **18**, 146, (1904).
[2] This JOURNAL, **23**, 96 (1900).
[3] *Loc. cit.*

spect to freezing-point lowerings as the corresponding chlorides.

When we turn to our results[1] for the nitrates of potassium, ammonium, sodium, and lithium, exactly the same relations appear. The first three have no water of crystallization, and give freezing-point lowerings of the same order of magnitude. Lithium nitrate crystallizes with 2.5 molecules of water, and gives much greater lowering than the three alkali nitrates in question.

In our earlier work we studied the sulphates[2] of sodium, potassium, and ammonium. Two of these have no water of crystallization, and the third, sodium sulphate, separates with varying amounts of water, or with none, depending upon the temperature.

The carbonates[3] of sodium and potassium were also studied in the first work that we did, and present an apparent exception to the above relation; sodium carbonate crystallizes with more water than potassium carbonate, yet shows a smaller lowering of the freezing-point. Sodium carbonate is however, strongly efflorescent, showing that it holds the ten molecules of water in unstable combination.

Turning to the work recorded in this paper, the number of exceptions is somewhat larger, although nearly all of the fifteen compounds crystallize with a large amount of water, as can be seen from the following table:

Table LII.

$MnCl_2.4H_2O$	$NiCl_2.6H_2O$	$CoCl_2.6H_2O$
$Mn(NO_3)_2.6H_2O$	$Ni(NO_3)_2.6H_2O$	$Co(NO_3)_2.6H_2O$
$MnSO_4.7H_2O$	$NiSO_4.7H_2O$	$CoSO_4.7H_2O$

$CuCl_2.2H_2O$	$AlCl_3.6H_2O$
$Cu(NO_3)_2.3H_2O$	$Al(NO_3)_3.8H_2O$
$CuSO_4.5H_2O$	$Al_2(SO_4)_3.9H_2O$

The sulphates all show much less lowering of the freezing-point than the corresponding chlorides and nitrates, notwithstanding the fact that they crystallize with more water than

[1] Ztschr. phys. Chem., 46, 281 (1903), Fig. IV. Phys. Rev., 18, 146 (1904).
[2] *Ibid.*, Fig. V.
[3] *Ibid.*, Fig. VI.

either of the other corresponding compounds. It must, however, be remembered that the sulphates in question are all binary electrolytes, while the chlorides and nitrates are ternary electrolytes, and, further, what is more important, the sulphates undoubtedly undergo polymerization in concentrated solutions, shown by the fact that such compounds as nickel sulphate, cobalt sulphate, and copper sulphate give, in such solutions, molecular lowerings that are much less than the constant for water. It is, therefore, impossible to say with how many molecules of water such sulphates are combined in solution, since we have these two influences—polymerization and possible hydration acting counter to one another at the same time, and no means of determining the magnitude of either in the presence of the other.

When we turn to the chlorides the only apparent exception is presented by cupric chloride, which is not closely allied chemically to the other chlorides. Manganese chloride with four molecules of water of crystallization gives less lowering than nickel and cobalt chlorides, each with six molecules of water of crystallization, the last two giving just about the same lowering. Aluminium chloride gives a much greater lowering than either nickel or cobalt chloride, although it contains the same number of molecules of water of crystallization. This would, however, be expected since aluminium chloride is a quarternary electrolyte, while the other two are binary electrolytes. The only apparent departure from our generalization in connection with these five chlorides is cupric chloride. It crystallizes with only two molecules of water, and yet gives about the same lowering, for comparable concentrations as nickel and cobalt chloride. Since cupric chloride differs so widely chemically from the other chlorides, it really should not be compared with them, and is, then, not a true exception. When we turn to the nitrates of the five elements studied in this part of our investigation, the relations are as satisfactory as those just discussed for the chlorides. Manganese nitrate, however, gives considerably less lowering than nickel and cobalt nitrates, although it contains the same number of molecules of water of crystallization. Nicke

nitrate and cobalt nitrate give about the same lowering, and have the same number of molecules of water of crystallization. Aluminium nitrate gives greater lowering than any other compound thus far studied. It crystallizes with eight molecules of water. At the great concentration employed it should be stated that hydrolysis has very little effect on our results, even in the case of the aluminium compounds.

Copper nitrate presents the only apparent exception among the five nitrates. It gives about the same lowering as the nitrates of nickel and cobalt, but crystallizes with only half as much water. For the reasons given above for copper chloride, it should not be brought into this comparison. It is then made evident from the above discussion that there is a *relation between the freezing-point lowering in concentrated solutions and the water of crystallization of the compound*. The number of cases that conform to this relation is so large, and the number of exceptions so small, that the agreement cannot be regarded as accidental.

This relation is strong evidence in favor of our theory that the *very great freezing-point lowerings in concentrated solutions is to be explained by the existence of hydrates in such solutions*. Other things being equal, those substances that crystallize from solution with the largest amounts of water, would be the ones that would combine with the largest amounts of water in solution. The amount of water with which a molecule of any substance can combine in a concentrated solution may, however, be much greater than that which it can carry with it from the solution in a stable form; may be much greater than its water of crystallization.

We have also seen that a large number of substances, indeed, practically all of the forty-nine compounds investigated, give lowerings of the freezing-point in concentrated solutions that are larger than those that would be calculated from their dissociation. Many of these compounds crystallize from such solutions without any water of crystallization. Our theory of the existence of hydrates in concentrated solutions applies as well to these as to other substances. These substances, as we have seen, do not show a molecular lowering as large as

those substances that have water of crystallization. This means that such substances do not combine in solution with as many molecules of water as those with water of crystallization. We would, therefore, not expect them to be able to hold, in a stable condition, as many molecules of water of crystallization outside of solution, as those substances which combine with a larger number of water molecules in solution, and such is the fact. Indeed, where they are combined with very few molecules of water in solution, as is shown by the freezing-point lowerings to be the case with a number of the compounds already studied, we would expect such compounds to separate from solution without any water of crystallization, and such is the fact.

Not a single one of the forty-nine compounds studied, which crystallizes from solution without water of crystallization shows very great lowering in concentrated solution. A better agreement between fact and theory could scarcely be asked.

It should, however, not be forgotten that while, in concentrated solutions of apparently almost all electrolytes, we have hydrates of greater or less complexity, we have also some of the molecules broken down into ions. This is shown by the fact that such solutions always conduct the electric current to a greater or less extent. The conductivity curves are, as we have seen, in all cases regular, with no sign of any minimum, showing that the dissociation proceeds regularly as we increase the dilution of the solution. The same observation applies to the refractivity curves. They are always perfectly regular from the most concentrated to the most dilute solution investigated.

Let us now see exactly what the minima in the freezing-point curves mean. Starting with the most dilute solution, the curves gradually fall with increase in concentration, due to the diminution of dissociation. Finally, a concentration is reached where the hydrates with a few molecules of water begin to form. These diminish the amount of water acting as solvent by just so much, and tend to increase the molecular lowering of the freezing-point. Finally, at a definite concentration for each substance, these two opposite influences are t

equal and we have the minimum in the curve. As the concentration becomes still greater more complex hydrates form, and this effect far overcomes the opposite effect due to diminishing dissociation, and the freezing-point curves rise. This influence becomes greater and greater, the greater the concentration, and the opposite influence, due to diminishing dissociation, becomes less and less, and the freezing-point curve continues to rise with the concentration, at least as far as the most concentrated solutions that we have studied.

Our theory thus accounts, in a most satisfactory manner, for the facts.

Calculation of the Composition of the Hydrates.

In order to calculate the exact composition of any hydrate in solution we must know, in addition to the facts recorded in this paper, the exact dissociation of a solution and its specific gravity. We must know the dissociation in order to determine the molecular lowering that would be produced if there was no hydration. We must know the specific gravity to determine the difference between the amount of water in a liter of the solution, and 1,000 grams of water, since molecular lowerings are all referred to 1,000 grams of water, and this difference is very considerable in solutions of such great concentration as some of those which we have used.

We have not had time as yet to obtain such data in many cases, but shall do so as soon as possible. It is not difficult to find good specific gravity measurements recorded for many substances, but these should be determined as near to 0° as possible, and the dissociation must be measured at zero.

We have already obtained the necessary data for cupric chloride and nitrate, and aluminium chloride and nitrate, and have calculated the composition of the hydrates formed by these substances at the various dilutions studied. The specific gravity data in the case of the aluminium salts are given in Tables XXXVIII., XLII., and XLVI., and the dissociations α are taken from Tables XXXVI. and XL. The specific gravity data for the copper salts are taken from the work of others, while the dissociations α (Tables XXIX. and

XXXII.) are calculated from our own conductivity measurements. In calculating the dissociations from conductivity it is necessary to know $\mu\infty$ at the same temperature that the values of μ_v were determined. This we have not yet had time to determine directly in the case of any substance studied in this or the preceding paper. We found that it would be impossible to determine this value directly in such cases as aluminium chloride and nitrate, on account of the great amount of hydrolysis that occurs in dilute solutions of such substances. We have, however, determined $\mu\infty$ for copper chloride and nitrate, and aluminium chloride and nitrate, indirectly, as follows:

From the freezing-point lowering of a dilute solution, α was calculated, knowing α and μ_v for a dilute solution, $\mu\infty$ was calculated at once; $\mu_v = \alpha\mu\infty$. This calculation was made for each substance, using three dilutions, and the values of $\mu\infty$ for the different dilutions in every case agreed to within a very few units. In the above calculation of $\mu\infty$ we were careful to select only those solutions that were of considerably greater dilution than that at which the minimum in the freezing-point curve manifested itself. In solutions near the freezing-point minimum there would probably still be a little hydration, and the value of α for such solutions, as calculated from freezing-point measurements, would contain some error.

Given the value of $\mu\infty$ for the salt at 0°, the dissociation at this temperature was calculated from our conductivity measurements in the usual way, $\alpha = \frac{\mu_v}{\mu\infty}$.

The dissociations at 0° cannot differ appreciably from the dissociations at the freezing-points of the various solutions, since Jones and Douglas[1] showed that the temperature coefficient of dissociation is practically 0, from 0° to 25°.

Given the above data, the calculation of the number of molecules of water combined with 1 molecule of the salt at any dilution is very simple, as would be gathered from an earlier part of this paper. In the first place, the "Observed

[1] This JOURNAL, 26, 428 (1901).

molecular lowering" was corrected for specific gravity, giving the "True molecular lowering." The molecular lowering that would be produced if there was no hydration was then calculated from the equation:

$$\frac{\text{Molecular lowering}}{1.86} = i;$$

$$\frac{i-1}{2} = \alpha \text{ for ternary electrolytes, } (CuCl_2, Cu(NO_3)_2);$$

$$\frac{i-1}{3} = \alpha \text{ for quaternary electrolytes, } (AlCl_3, Al(NO_3)_3).$$

The ratio of the molecular lowering calculated, to the molecular lowering found, multiplied by 1,000, gave the amount of water that was present in 1,000 cc. of the solution as water playing the rôle of solvent. The difference between this amount of water and 1,000 grams was the amount that had combined with 1 gram-molecular weight of the salt, under the conditions present in the solution in question.

Knowing the amount of water in grams that had entered into combination, we determined the number of gram-molecular weights of water by dividing by 18, and this gives us at once the number of molecules of water combined with 1 molecule of the salt in the solution in question.

The results for copper chloride, copper nitrate, aluminium chloride, and aluminium nitrate are given below in Tables LIII. to LVI. m is the concentration in gram-molecular normal, α the dissociation of the solution, L the calculated molecular lowering, $\frac{\Delta}{m}$ the observed molecular lowering, $\frac{\Delta'}{m}$ the corrected or true molecular lowering, m' the number of gram-molecules of water combined with the dissolved substance. These results are plotted in curves, Fig. XVIII., the ordinates representing number of gram-molecules of water combined with the dissolved substance, and the abscissæ concentration of the solution.

A glance at the tables, LIII. to LVI. or the curves in Fig. XVIII., will show that the amount of water combined with 1 molecule of the dissolved substance is greatest in the most

Table LIII.—Copper Chloride.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.602	0.137	2.39	8.00	7.65	38.2
2.0816	0.187	2.58	7.43	7.24	35.7
1.8210	0.212	2.68	7.12	6.96	34.2
1.5612	0.238	2.77	6.65	6.48	31.8
1.3010	0.292	3.20	6.45	6.32	27.4
0.7806	0.359	3.23	5.65	5.08	20.2

Table LIV.—Copper Nitrate.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.36	0.172	2.53	9.26	8.21	38.4
1.89	0.231	2.75	8.20	7.55	35.3
1.65	0.263	2.87	7.07	5.87	28.4
1.18	0.337	3.15	6.60	6.34	11.0

Table LV.—Aluminium Chloride.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
2.124	0.177	2.88	21.18	19.32	48.1
1.593	0.237	3.22	14.98	14.15	43.7
1.434	0.253	3.31	13.60	13.10	42.0
1.195	0.312	3.64	11.40	11.00	37.2
0.876	0.388	4.07	9.09	8.84	30.0
0.657	0.435	4.33	7.79	7.63	24.0
0.531	0.476	4.56	7.21	7.10	19.8
0.398	0.529	4.86	6.52	6.45	13.7
0.299	0.570	4.91	6.15	5.63	7.1
0.200[1]	0.620	5.38	5.74	5.71	3.3

Table LVI.—Aluminium Nitrate.

m.	a.	L.	$\frac{\Delta}{m}$.	$\frac{\Delta'}{m}$.	m'.
0.066	0.306	3.61	11.06	10.36	36.2
0.853	0.366	3.94	9.60	9.12	31.6
0.746	0.407	4.17	9.06	8.68	29.0
0.533	0.478	4.58	8.00	7.77	23.5
0.320	0.564	5.06	7.15	7.02	15.5
0.213	0.621	5.38	6.57	5.78	3.8

[1] We convinced ourselves that in this determination it was ice and not the solid salt that separated, as follows: As more and more of the solid separated the thermometer sank lower and lower, going down from —45°, the true freezing-point, gradually to —50°. This could not have occurred if the salt was separating either as such or as a hydrate, since the hydrate that would separate could not carry more water with it out of solution than the quantity with which it was combined in solution.

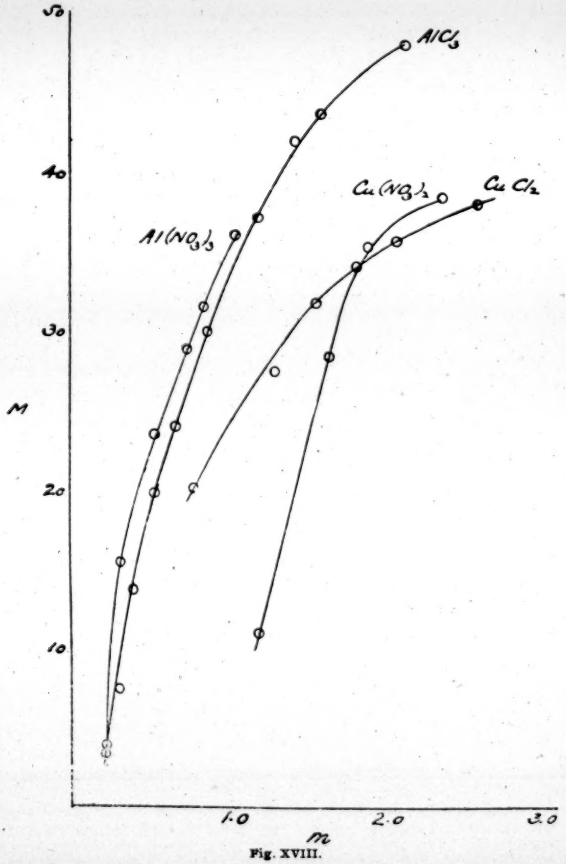


Fig. XVIII.

concentrated solution employed, and becomes less and less as the dilution of the solution increases. The regularity of the

curves expressing the relation between concentration of the solution and composition of the hydrates, is really surprising when we consider the number of experimentally determined quantities involved in every point on the curve. There are no less than four such quantities: (1) The concentration of the solution; (2) the lowering of the freezing-point; (3) the specific gravity of the solutions; (4) the dissociation of the solutions. Quantities (1) and (3) can be measured very accurately. Quantity (2) can be determined with a fair degree of accuracy, but in the most concentrated solutions that we studied there is necessarily some appreciable error involved in measuring the freezing-points. Quantity (4) is the most difficult to measure accurately for such substances as those given in Fig. XVIII., since it involves both the freezing-point and conductivity methods. As has been pointed out, $\mu\infty$ for aluminium chloride and nitrate cannot be determined directly by the conductivity method, on account of the hydrolytic dissociation in dilute solutions. But by continuing the conductivity and freezing-point methods the approximate value of $\mu\infty$ at 0° could be obtained. The values of α, involving these values of $\mu\infty$, may, therefore, contain a not inappreciable error.

However, notwithstanding all of these facts, the curves came out as smoothly as could be expected, if they contained only one or two experimentally determined values.

The fact that the amount of water combined with 1 molecule of the salt is greatest in the most concentrated solution, and becomes less and less as the dilution is increased, is just what we would expect. In the dilute solutions there is no evidence of the existence of hydrates. Indeed, there is strong evidence that hydrates of any considerable complexity do not exist. The dissociation of dilute solutions can be measured by the freezing-point method, and also by the conductivity method, and the two methods give the same results within the limits of experimental error. It is impossible that the same results should be obtained from the two methods if there were complex hydrates formed in the dilute solutions.

It is worth while calling attention again, at this point, to

the relation between the complexity of the hydrate formed in solution and the number of molecules of water with which the substance in question crystallizes, since it is so apparent from Fig. XVIII. Aluminium nitrate crystallizes from solution with 8 molecules of water. It contains more water of crystallization in stable combination than any salt that we have studied, with the exception of aluminium sulphate, and we have seen that the sulphates show polymerization in concentrated solutions.

Aluminium chloride and nitrate give greater lowerings of the freezing-point than any other substances that we have studied, and, therefore, form more complex hydrates in concentrated solution than any other substance investigated. Such a general relation is almost more than we could expect, and yet it undoubtedly exists.

Do the Molecules or the Ions Form the Hydrates?

It is difficult to say with certainty whether it is the molecules or the ions, or both, that form the hydrates in concentrated solutions, since all such solutions that we have studied contain both molecules and ions. Since, however, those solutions that are most concentrated, and, therefore, the least dissociated, show the greatest amount of hydration, it seems probable that it is the molecules and not the ions that combine with water and form hydrates. This conclusion is further strengthened by the fact that in the dilute solutions where the number of ions relative to the number of molecules is large, there is little if any hydration.

Taking both of these facts into account, it becomes highly probable that it is the molecules and not the ions that combine with water, forming the hydrates.

Relation to the Work of Roozeboom.

The above results, especially those with aluminium chloride, which have been worked out fully, recall the beautiful investigations of Roozeboom on calcium chloride[1] and ferric chloride.[2] Roozeboom showed that each of these substances

[1] Ztschr. phys. Chem., 4, 31 (1889).
[2] *Ibid.*, 10, 477 (1892).

is capable of forming a number of definite hydrates with water, in very concentrated solutions. This, of course, does not prove that such substances form hydrates at the much greater dilutions at which we worked, but is quite in keeping with our theory, and, indeed, furnishes circumstantial evidence in its favor.

Summary.

1. Of the forty-nine electrolytes that we have studied, thirty-nine show a minimum in the freezing-point curve. Nearly all of the forty-nine compounds, whether they do or do not show such a minimum, give too great lowering of the freezing-point of water in concentrated solutions, as calculated from their dissociation, except a few sulphates which were shown to be polymerized in such solutions.

2. The boiling-point curves, as far as they have been worked out, also show a minimum, but this occurs at greater concentration than in the corresponding freezing-point curve.

3. The conductivity curves and the refractivity curves show no sign of a minimum, not even in the regions of concentration where the freezing-point minima and boiling-point minima occur.

4. The theory that has been advanced to account for all of the facts is that in such concentrated solutions the dissolved substance combines with the solvent, forming hydrates. These exist in concentrated solutions together with a relatively small number of ions resulting from the electrolytic dissociation of the salt.

5. It was pointed out that if such hydrates exist in solution, those substances that crystallize from such solutions with the largest amount of water of crystallization, would be the substances, *cæteris paribus*, that we would expect to form the most complex hydrates in such solutions.

6. A careful study of this relation was made, comparing those substances which could reasonably be expected to come within its scope. The comparison would, of course, be limited to the salts of any given acid and to the metals of any given group, or at most to the metals of correlated groups.

The result is that of the thirty-eight substances thus far studied, which have water of crystallization, there is only one apparent exception to this relation, and that exception is not clean cut.

7. It was further pointed out that the fact that the boiling-point minimum occurs at greater concentration than the freezing-point minimum argues strongly in favor of our theory. The hydrates in solution would be less stable at the higher temperature, and, therefore, a greater concentration would be required for their production.

8. Every one of the forty-nine substances studied that crystallizes without water of crystallization, gives relatively small lowering of the freezing-point in concentrated solution, but nearly every one at the same time gives a lowering that is too great as calculated from its dissociation. These substances, therefore, like those that crystallize with water of crystallization, form hydrates in concentrated solutions, but the hydrates contain much less water, just as we would expect.

9. A freezing-point curve was then carefully studied, and the exact significance of the minimum pointed out—it is the concentration at which the diminishing dissociation is just counterbalanced by the increasing formation of the hydrates with increasing concentration.

10. The composition of the hydrates was then calculated in those cases where sufficient data have already been obtained, and it was found that the hydrates decrease regularly in complexity with the dilution, (Fig. XVIII.) disappearing entirely at a dilution greater than that at which the freezing-point minimum occurs. The regularity of the curves that were obtained is surprising, considering the number of quantities experimentally determined, that is involved in each point on the curve.

11. Evidence was furnished, indicating that it is the molecules and not the ions, that form the hydrates in concentrated solutions.

Conclusion.

The accusation has been made against the modern theory

of solution, especially by those who do not worship at the shrine of the ion, that it applies only to dilute solutions, and there is a certain justification for the criticism. It has been claimed that the laws of gas-pressure apply only to dilute solutions, and from the data available it seemed that such was the case.

We believe that the explanation of this apparent discrepancy is now at hand. In concentrated solutions a part of the solvent is combined with the dissolved substance, and such solutions are, therefore, more concentrated than they would appear to be from the amount of dissolved substance present in them. When this is taken into account it will probably be shown that the gas laws apply to concentrated solutions as well as to dilute. In making such applications it will probably be necessary to take into account also such factors as appear in Van der Waals' equation for gases, but this would only render still more nearly parallel the gaseous condition and the condition of the dissolved substance.

We shall extend this work as rapidly as possible, bringing a much wider range of substances within its scope, and obtaining such data as are still necessary in order to be able to calculate the composition of the hydrates formed by those substances whose freezing-point lowerings we have already studied, and the change in the composition of such hydrates with change in dilution.

We shall later take up a systematic study of the non-electrolytes from this same standpoint. It is already known that many such substances show abnormally great lowering of the freezing-point of water in concentrated solutions. A systematic study of this field from the standpoint recorded in this paper will probably show that these substances, like the electrolytes, also combine with water in concentrated solutions. This problem also we shall take up as soon as possible.

In conclusion, we wish to thank the Carnegie Institution for the grant which has made possible the rapid prosecution of this work.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1904.

Contributions from the Chemical Laboratory of Harvard College.

ON TETRACHLORDINITROBENZOL.

By C. Loring Jackson and H. A. Carlton.

Our object in undertaking the work described in this paper was to study the behavior of trichlortrinitrobenzol with various reagents. This substance was prepared by Dr. J. F. Wing,[1] in this laboratory, in 1887, without difficulty, but all attempts to make it in recent years have led to low melting products, from which no trichlortrinitrobenzol could be isolated. It was evident that some condition necessary to the formation of the trichlortrinitrobenzol had been overlooked, but even after consultation with Dr. Wing we were unable to recall this condition. Finally, after many experiments, it was found that the missing condition was the use of a return-condenser during the boiling of the trichlordinitrobenzol with nitric and sulphuric acids instead of closing the flask with a porcelain crucible or glass bulb as in the later experiments. With this precaution the trichlortrinitrobenzol becomes again an easily accessible substance.

In the meantime, however, we had turned our attention to the tetrachlordinitrobenzol,[2] as we thought from our experience with the tribromtrinitrobenzol that this might be the impurity formed in our unsuccessful attempts to make the trinitro body, and by the time we had overcome the difficulty in the way of making the trinitro compound we had advanced so far in our work on the tetrachlordinitrobenzol that it was wiser to leave the study of trichlortrinitrobenzol to others.[3]

The tetrachlordinitrobenzol, $C_6Cl_4(NO_2)_2$, was made from unsymmetrical tetrachlorbenzol, and must therefore have the structure $Cl_4$1,3,5,6.$(NO_2)_2$2,4. It melts at 162° and is a decidedly reactive body. With aniline, at 100°, it is converted into the chlortrianilinodinitrobenzol, $C_6(C_6H_5NH)_2Cl(NO_2)_2$, which has a dark red color, melts at 179°, and forms no salts. The constitution of this substance was determined by preparing the tribromchlordinitrobenzol (which melts at 208°) from

[1] This Journal, 9, 354 (1887).

[2] This Journal, 10, 291 (1888).

[3] The results of the work on trichlortrinitrobenzol will be published soon in a paper by P. S. Smith and one of us.

ordinary tribromaniline, and treating it with aniline, when it gave the same chlortrianilinodinitrobenzol melting at 179°, thus proving that its structure was

$$(C_6H_5NH)_3,1,3,5.Cl_3,(NO_2)_2,2,4,$$

so that the behavior of the tetrachlor compound is the same in this respect as that of the tetrabromdinitrobenzol.[1]

The trichloranilinodinitrobenzol has a most uncommonly strong tendency to form addition-compounds, similar, apparently, to salts with water of crystallization. They were formed by crystallizing the trianiline compound from various solvents, and with the exception of the chloroform compound, were stable in the air or *in vacuo*, but lost the added substance at 100°. A number of substances of this class were prepared, and analyzed, $C_6(Cl_4H_3NH)_3Cl(NO_2)_2C_6H_6$, dark-red, rhombic plates, made by crystallization from benzol. If the crystallization took place from a mixture of ligroin with the smallest possible amount of benzol, orange needles were obtained mixed with some red needles. The orange body gave a loss corresponding to $[C_6(C_6H_5NH)_3Cl(NO_2)_2]_2C_6H_6$. The amount of substance used was so small that we cannot accept this result without additional evidence, but we think this formula may be adopted for the following reasons: The substance was formed when much less benzol was used than that necessary for the red compound just described, and the toluol compound containing 2 molecules of the trianilino compound to 1 of toluol is also orange and crystallizes in needles. It is possible that this compound is an addition-product with the hydrocarbons of the ligroin instead of with benzol, but this does not seem probable to us. We did not provide better analytical results because of the difficulty in separating these orange needles from the red crystals formed with them, which could be done only by mechanical separation. Our attempts to get the red needles in a state of purity failed completely, but an analysis of a mixture of red and orange crystals gave so small a loss that we think these red needles must be the chlortrianilinodinitrobenzol itself.

[1] This JOURNAL, 12, 294 (1890).

The toluol compound, $[C_6(C_6H_5NH)_3Cl(NO_2)]_2C_7H_8$, formed orange needles. This acetic acid compound was

$$C_6(C_6H_5NH)_3Cl(NO_2)_2C_2H_4O_2,$$

long orange needles; the chloroform compound,

$$C_6(C_6H_5NH)_3Cl(NO_2)_2CHCl_3,$$

long, dark red narrow prisms. This was the only one of these compounds not permanent in the air. Herman and one of us[1] obtained a similar compound,

$$C_6H(C_6H_5NH)_3(NO_2)_2CHCl_3,$$

from trianilinodinitrobenzol, but in that work no compound with benzol was observed, and, as the experiments were carried on with care, it seems improbable that one was overlooked.

It was of interest to determine whether the chlortrianilinodinitrobenzol, or rather its addition-compounds occurred in two modifications differing in color like those of the trianilinodinitrobenzol described in the paper just cited. The case of the red and orange needles obtained by crystallizing chlortrianilinodinitrobenzol from ligroin and a little benzol has been discussed already. The acetic acid compound also, when it was first prepared, contained a few red crystals mixed with the orange needles, but all attempts to purify these red needles failed, so we can give no answer to this question.

The action of sodic ethylate on the tetrachlordinitrobenzol consists of two simultaneous reactions. In one three of the atoms of chlorine are replaced by three ethoxy groups,

$$C_6Cl_4(NO_2)_2 + 3C_2H_5ONa = C_6(C_2H_5O)3Cl(NO_2)_2 + 3NaCl,$$

forming what is without much doubt a chlordinitrophloroglucine triethylether, melting at 76°, or the diethylether, $C_6(C_2H_5O)_2OHCl(NO_2)_2$, melting at 102°–103. In the other the two nitro groups are replaced by the two ethoxy groups,

$$C_6Cl_4(NO_2)_2 + 2C_2H_5ONa = C_6Cl_4(C_2H_5O)_2 + 2NaNO_2,$$

forming tetrachlorresorcine diethylether, melting at 73°. In this respect the behavior of the tetrachlordinitrobenzol with

[1] This JOURNAL, 16, 39 (1894).

sodic ethylate is similar to that of tribromtrinitrobenzol,[1] and probably to that of the tetrabromdinitrobenzol,[2] as the formation of the resorcine ether from this substance has been established, and although the phloroglucine ether has not been isolated, it was undoubtedly formed. There is, however, a marked difference in the behavior of the tetrachlor- and the tetrabromdinitrobenzols, as the latter forms with sodic ethylate $C_6Br_3NO_2(C_2H_5O)_2$, by the replacement of an atom of bromine and a nitro group, instead of undergoing the replacement of both nitro groups, as is the case of the tetrachlor body; this difference is undoubtedly caused by the weaker attraction of bromine than chlorine for the benzol ring.

Our observations seemed to show that more of the resorcine ether was formed, when the action took place with the aid of heat than in the cold, but this point cannot be considered established until experiments have been tried which are parallel in every other respect. It should also be noted that our work with sodic ethylate has been directed toward the isolation of the principal products of the reaction, not to the identification of all its products.

With sodic malonic ester the tetrachlordinitrobenzol gave trichlordinitrophenylmalonic ester,

$$C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2,$$

melting at 82°, but if the crude product of the reaction was distilled with steam, the residue contained a substance melting at 87°–88°, which gave numbers on analysis corresponding to those for trichlordinitrophenylacetic ester,

$$C_6Cl_3(NO_2)_2CH_2COOC_2H_5,$$

and this yielded on saponification a body analyzing for the trichlordinitrophenylacetic acid, $C_6Cl_3(NO_2)_2CH_2COOH$, and melting at 190°–191°. We have adopted these names for these compounds provisionally, but the second substance differs so much from a substituted acetic acid in its properties that more experimental work is needed on this subject before it can be considered that the value of these bodies is deter-

[1] Jackson and Warren: This JOURNAL, 15, 608 (1893).
[2] Jackson and Calvert: *Ibid.*, 18, 311 (1896).

mined with certainty. The most marked peculiarity of this substance is that it does not dissolve in cold aqueous sodic hydrate even with the assistance of a few drops of alcohol, which could hardly be the case if it were an acetic acid. On the other hand, hot sodic or ammonic hydrate forms with it yellow solutions of its salts. It is also unusually stable when boiled with alcohol, showing no tendency to form the ethyl ester like the dichlordinitrophenylacetic acid,[1] or to drop into a substituted toluol under these conditions like the bromdinitrophenylacetic acid.[2] Nor are these peculiarities confined to the substituted acetic acids, since trichlordinitrophenylmalonic ester shows only a very slight tendency to form salts, the trichlordinitrophenylacetic ester none at all, whereas all the other compounds of these classes, which have been studied in this laboratory, form salts very easily. These differences in behavior may be due to the fact that the side chain occupies a different position on the ring in these compounds, or to differences in the side chains themselves, but the real cause of these differences cannot be made out until the constitution of our new compounds has been determined.

Attention is called in the experimental part of the work to some remarkable differences in the amount of heat given off in the reactions of the tetrachlordinitrobenzol with sodic ethylate and with sodic molonic ester as compared with the corresponding reactions with the tetrabromdinitrobenzol, but it is not worth while to discuss these anomalies at present, as the observations were made by different men at considerable intervals of time, and cannot be looked on as established, until they rest on experiments parallel in every respect.

Upon comparing the reaction of the tetrachlordinitrobenzol and sodic malonic ester with the corresponding reaction of tetrabromdinitrobenzol an important difference appears. With the bromine compound 1 atom of bromine is replaced by the malonic ester group and another by hydrogen, forming dibromdinitrophenylmalonic ester, $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$, while with the chlorine compound the action stops at the replacement of 1 atom of chlorine by the malonic ester group,

[1] Jackson and Lamar: This JOURNAL, 18, 682 (1896).
[2] Jackson and Robinson: *Ibid.*, 11, 551 (1889).

the strange replacement of halogen by hydrogen not taking place, so that the product is

$$C_6Cl_3(NO_2)_3CH(COOC_2H_5)_2.$$

This result was not unexpected, as no such replacement of chlorine by hydrogen has been observed as yet.

EXPERIMENTAL PART.

Preparation of Trichlortrinitrobenzol.

The preparation was carried on as follows: One gram of trichlordinitrobenzol[1] was boiled vigorously for about eight hours in a very long-necked flask with a mixture of 25 cc. of commercial fuming nitric acid of sp. gr. 1.5 and 10 cc. of sulphuric acid of sp. gr. 1.876. The nitric acid used was nearly colorless; an acid, which owed its high specific gravity to nitrous fumes, would probably not act at all. On cooling, part of the product crystallized out, and the whole was precipitated by pouring the mixture into cold water. The crude precipitate melted at 115°, but one crystallization from alcohol raised it to 185°, and further crystallization brought it to the constant melting-point, 187°, showing that it was the desired symmetrical trichlortrinitrobenzol.

Preparation of Tetrachlordinitrobenzol.

$C_6Cl_4(NO_2)_2$,Cl_4,1,3,5,6.$(NO_2)_2$,2,4.—This substance was made from trichloraniline prepared according to Victor Meyer and Sudborough,[2] as follows: One hundred grams of freshly distilled aniline were dissolved in a kilogram of chloroform, which had been washed until free from alcohol and thoroughly dried with calcic chloride. A stream of dry chlorine was passed through the mixture for about thirty hours, the vessel being kept cold by immersion in ice-water. The precipitate formed was filtered out, dried, and washed with water. Yield of trichloraniline 116 grams from 100 grams of aniline, that is 55 per cent of the theoretical yield.

The trichloraniline was converted into tetrachlorbenzol by Sandmeyer's reaction. Twenty grams of trichloraniline were

[1] Jackson and Lamar: This JOURNAL, **18**, 666 (1896).
[2] Ber. d. chem. Ges., **27**, 3151 (1894).

mixed with 120 cc. of strong hydrochloric acid in an Erlenmeyer flask, and 20 grams of powdered sodic nitrite added in small portions at a time, the flask being closed with a glass bulb, and immersed in cold water. When all of the sodic nitrite had been added, the dark brown solution of the diazo compound was treated with 40 grams of cuprous chloride, which caused a considerable effervescence accompanied by a great rise in temperature. After the effervescence had ceased the flask was heated on the steam-bath for two or three minutes. As the solution cooled, part of the tetrachlorbenzol was deposited as a mass of tarry needles. The whole of it was then precipitated by the addition of a large amount of cold water, and purified by crystallization from alcohol.

Twenty grams of trichloranile gave 13.5 grams of tetrachlorbenzol, a yield of 61 per cent of the theoretical.

The tetrachlorbenzol was converted into tetrachlordinitrobenzol, as follows: Twenty grams of it were boiled with a mixture of 200 cc. of fuming nitric acid of sp. gr. 1.5 and 80 cc. of sulphuric acid of sp. gr. 1.84 in an Erlenmeyer flask closed by a loosely fitting glass bulb. After vigorous boiling for half an hour the tetrachlordinitrobenzol began to separate, but disregarding this, the boiling was continued for half an hour longer, and then the contents of the flask were poured into a large amount of cold water. The precipitate thus obtained was crystallized from 90 per cent acetic acid, until it showed the constant melting-point 162°, when it was dried at 100° and analyzed with the following results:

I. 0.1850 gram substance gave, by the Carius method, 0.3496 gram AgCl.

II. 0.1958 gram substance gave 0.3701 gram AgCl.

III. 0.2044 gram substance gave 0.3850 gram AgCl.

IV. 0.1845 gram substance gave 15.3 cc. moist N_2 at 21° and 762 mm.

	Calculated for $C_6Cl_4(NO_2)_2$.	Found. I.	II.	III.	IV.
Cl	46.40	46.72	46.73	46.59	....
N	9.15	....	....	....	9.46

There is no doubt, therefore, that the substance is a tetra-

chlordinitrobenzol and the method of preparation settles its constitution as $Cl_1 1,3,5,6.(NO_2)_2 2,4$.

Properties of Tetrachlorainitrobenzol. — It crystallizes in thick, white, rhombic plates, which seem to be prisms with much developed basal planes. In some cases each obtuse angle is truncated by a plane, more usually it is bevelled by two planes at a still more obtuse angle. It melts at 162°, and is freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; slightly soluble in cold glacial acetic acid, freely soluble in it when hot; essentially insoluble in cold, and only slightly soluble in hot ethyl alcohol; insoluble in water. The best solvent for it is 90 per cent hot acetic acid. It is not affected by the three strong acids or sodic hydrate. It is a decidedly stable substance, as heating to 300° for two days with fuming nitric acid was necessary to decompose it, and it can be heated to its boiling-point without decomposition, and is decomposed only very slowly by prolonged boiling.

Action of Aniline on Tetrachlordinitrobenzol.

Chlortrianilinoditrobenzol, $C_6(C_6H_5NH)_3Cl(NO_2)_2$. — Five grams of tetrachlordinitrobenzol were mixed with 50 grams of freshly distilled aniline, and heated on the steam-bath. The cold aniline dissolved but little of the tetrachlordinitrobenzol, on heating for a short time, however, the whole dissolved with a red color, which grew much darker as the heating continued. The large excess of aniline was necessary to keep the substance in solution. After heating for three hours the product was allowed to cool, when a mass of dark red needles was deposited. The excess of aniline was removed by treatment with dilute hydrochloric acid and the dark red residue filtered off, washed thoroughly with water, and purified by crystallization from a mixture of ligroin and benzol, until it showed the constant melting-point 179°, when it was dried at 100° and analyzed with the following result:

I. 0.1958 gram substance gave, by the Carius method, 0.0604 gram AgCl.

II. 0.1971 gram substance gave 26.2 cc. of moist N_2 at 28° and 770 mm.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2$.	Found. I.	II.
Cl	7.46	7.63	....
N	14.72	....	14.79

The substance is therefore the chlortrianilinodinitrobenzol formed by replacing three of the atoms of chlorine by three aniline groups.

Properties of the Chlortrianilinodinitrobenzol.—We are unable to give the crystalline form of this substance, as it is separated from each of the solutions tried by us in the form of an addition-compound with the solvent. From a mixture of much ligroin with little benzol a few red needles were obtained, which may have been the chlortrianilinodinitrobenzol, but we were unable to prove that this was the case. It has a dark red color, and melts at 179°. It is freely soluble in ether, chloroform, acetone, or carbonic disulphide ; soluble in cold benzol, or glacial acetic acid, freely soluble in these solvents, when hot ; slightly soluble in ethyl alcohol, whether cold or hot, somewhat more soluble in methyl alcohol ; insoluble in cold ligroin, only slightly soluble in it when hot ; insoluble in water. There is no good solvent for it on account of its tendency to combine with the most various solvents. Aniline or acetol also dissolves it, but seems to form addition-compounds like the other solvents studied. Neither strong hydrochloric acid, nor strong nitric acid has any apparent action on it. A more particular account of its behavior with hydrochloric acid is given later. Strong sulphuric acid decomposes it even in the cold. Sodic hydrate in aqueous solution has no action on it. Further treatment with aniline failed to remove the fourth atom of chlorine. Its most striking property is its very strong tendency to form addition-compounds, in which the added body seems to have the same function as water of crystallization. Some of these substances are described below.

Compounds of Chlortrianilinodinitrobenzol with Benzol.

$C_6(C_6H_5NH)_3Cl(NO_2)_2C_6H_6$.—This substance, obtained by crystallizing chlortrianilinodinitrobenzol from benzol, gave the following results on analysis :

I. 0.3373 gram of the air-dried substance, when heated to 100°, lost 0.0475 gram.

II. 0.3435 gram lost 0.0485 gram.

III. 0.2026 gram of substance dried *in vacuo* gave 23.5 cc. of moist N_2 at a temperature of 26° and a pressure of 755 mm.

IV. 0.1709 gram of substance dried *in vacuo* gave, by the Carius method, 0.0450 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_2(NO_2)_2C_6H_6$.	Found. I.	II.	III.	IV.
C_6H_6	14.09	14.08	14.11	....	....
N	12.65	....	....	12.79	....
Cl	6.41	....	....	....	6.57

There can be no doubt therefore that the substance is composed of one molecule of the chlortrianilinodinitrobenzol and one of benzol.

Properties.—It forms dark crimson rhombic plates. It melts at the same temperature as the chlortrianilinodinitrobenzol, 179°, as it is broken up by heat. At ordinary temperatures it is decidedly stable, losing its benzol very slowly even *in vacuo*, but at a temperature of 100° drives off the benzol completely. It seems to be rather less soluble in benzol than the chlortrianilinodinitrobenzol. Other solvents decompose it, giving the addition-compound with the substance used.

$[C_6(C_6H_5NH)_2Cl(NO_2)]_2C_6H_6$.—If the chlortrianilinodinitrobenzol was crystallized from a mixture of benzol and ligroin, orange crystals were obtained, mixed with a dark red substance, and, if the amount of benzol was reduced so that there was barely enough to effect the solution, the crystals were nearly all of the orange form. These orange needles were separated mechanically from the few red needles with which they were mixed, and analyzed with the following result:

0.1310 gram air-dried substance, when heated to 100°, lost 0.0103 gram.

	Calculated for $[C_6(C_6H_5NH)_2Cl(NO_2)_2]_2C_6H_6$.	Found.
C_6H_6	7.58	7.86

This analysis cannot be accepted as establishing with certainty the existence of the compound of 2 molecules of the

anilino body with 1 of benzol. In the first place the amount of substance used was so small that the analysis must be regarded with suspicion, and the difficulty of obtaining it was so great that we have not repeated it with larger quantities. Secondly, it is possible that this compound contains a paraffin hydrocarbon from the ligroin instead of benzol, but we think that the formula given above may be accepted for this substance with safety in view of the strong similarity between it and the toluol compound, which follows, whose composition has been established with certainty. The red crystals obtained from benzol and ligroin seemed to be crystals of

$$C_6(C_6H_5NH)_3Cl(NO_2)_3,$$

to judge from an analysis of a mixture of them and the orange substance, but we could not get them pure enough to settle this point.

Compound of Chlortrianilinodinitrobenzol with Toluol, $(C_6(C_6H_5NH)_3Cl(NO_2)_2)_2C_7H_8$.—This substance, prepared by crystallizing the trianilino body from toluol, gave the following results on analysis:

I. 0.3386 gram air-dried substance, when heated to 120°, lost 0.0306 gram.

II. 0.3222 gram substance lost 0.0287 gram.

III. 0.3410 gram substance lost 0.0308 gram.

	Calculated for $(C_6Cl(C_6H_5NH)_3(NO_2)_2)_2C_7H_8$.	Found. I.	II.	III.
C_7H_8	8.82	9.04	8.90	9.03

The substance is therefore a compound of 2 molecules of the anilino body wtih 1 of toluol. The compound

$$C_6(C_6H_5NH)_3Cl(NO_2)_2C_7H_8$$

would contain 16.21 per cent of toluol. That it has a constant composition is shown by the fact that two of the analyses (I. and III.) were made with samples from different preparations.

Properties.—It crystallizes in clusters of brilliant orange needles, which are stable at ordinary temperatures, since 0.3386 gram of the substance lost nothing on standing for a

day in the air, and only 0.0010 gram after two days *in vacuo*. When heated it loses its toluol, the color changing from orange to the dark red of the chlortrianilinodinitrobenzol. The toluol was identified by its smell and combustibility. It is somewhat less soluble in toluol than the mother substance. This compound, like all the other addition-compounds described in this paper, cannot be obtained by allowing the solvent to stand with the solid chlortrianilinodinitrobenzol, but appears only when it is crystallized from a solution.

Compound of Chlortrianilinodinitrobenzol with Acetic Acid, $C_6(C_6H_5NH)_3Cl(NO_2)_2C_2H_4O_2$.—This substance was made by crystallizing the anilino body from glacial acetic acid. It could also be obtained from the benzol addition-compound by crystallization from glacial acetic acid. The product consisted principally of long, orange needles mixed with a small amount of red needles, from which they were separated mechanically, and analyzed with the following results:

I. 0.3465 gram air-dried substance, when heated to 130°, lost 0.363 gram.

II. 0.1390 gram substance lost 0.0159 gram.

III. 0.3303 gram substance lost 0.0353 gram.

IV. 0.3305 gram substance lost 0.0381 gram.

V. 0.1720 gram air-dried substance gave, by the Carius method, 0.0471 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_3(NO_2)_2C_2H_4O_2$.	Found. I.	II.	III.	IV.	V.
$C_2H_4O_2$	11.20	10.47	11.44	10.69	11.53	....
Cl	6.62	....	....	....	....	6.77

The substance is therefore formed by the union of 1 molecule of acetic acid with 1 of the chlortrianilinodinitrobenzol. In order to show that the heat acted only by driving off the acetic acid, the residue dried at 130° was analyzed with the following result:

0.1780 gram substance gave, by the Carius method, 0.0542 gram AgCl.

	Calculated for $C_6Cl(C_6H_5NH)_3(NO_2)_2$.	Found.
Cl	7.46	7.53

An attempt was also made to isolate the red needles formed with the orange crystals on crystallizing chlortrianilinodinitrobenzol from acetic acid. They were carefully mixed out from the mixture and recrystallized from a small amount of acetic acid, but the product again consisted of a mixture of orange and red needles, so that in spite of repeated efforts we did not succeed in getting the red product pure. We cannot, therefore, decide definitely the question, whether this acetic acid compound occurs in two modifications. One opinion is that the orange body is the only form, the red crystals being probably the chlortrianilinodinitrobenzol without acetic acid of crystallization, and this view is supported by the fact that, if crystallized in a beaker, most of the product consists of the orange needles. If, on the other hand, it is crystallized in a watch-glass, where portions of it crystallizes in contact with less acetic acid, the red crystals are formed in considerable quantity.

Properties of $C_6(C_6H_5NH)_2Cl(NO_2)_2C_2H_4O_2$.—It crystallizes in long, orange needles, and is stable at ordinary temperatures, but loses its acetic acid rapidly when heated, changing color from orange to dark red. It is less soluble in acetic acid than the mother-substance. Other solvents decompose it, giving the compound of the anilino body with the solvent used.

Compound of Chlortrianilinodinitrobenzol with Chloroform, $C_6(C_6H_5NH)_2Cl(NO_2)_2CHCl_3$.—This substance was prepared by crystallizing the chlortrianilinodinitrobenzol from chloroform, to which a little ligroin had been added, as it comes down as a varnish, if chloroform alone is used. As it proved to be decidedly unstable, it was prepared for analysis simply by pressure in filter-paper.

I. 0.2845 gram substance, when heated to 100°, lost 0.0520 gram.

II. 0.4165 gram substance lost 0.0906 gram.

III. 0.3389 gram substance lost 0.0624 gram.

IV. 0.1283 gram substance lost 0.0253 gram.

	Calculated for $C_6(C_6H_5NH)_2Cl(NO_2)_2CHCl_3$.	Found. I.	II.	III.	IV.
$CHCl_3$	20.08	18.28	21.75	18.41	19.72

These analyses leave much to be desired, but are perhaps as near as could be expected with a substance that gives off chloroform rapidly at ordinary temperatures. They leave no doubt as to the formula of the substance. We may add that the presence of the chloroform in it was proved by the isonitrile test with aniline and sodic hydrate.

Properties of $C_6(C_6H_5NH)_3Cl(NO)_3CHCl_3$.—It crystallizes from chloroform in dark-red, long, narrow prisms, terminated at each end by two planes at a right angle to each other. It is the least stable of these compounds studied by us, since it gives off chloroform even at ordinary temperatures. It is less soluble in chloroform than the mother-substance. Other solvents decompose it, giving the compound with the solvent used.

Attempts to Prepare the Chloride of Chlortrianilinodinitrobenzol.—Although substances closely related to this do not usually give chlorides, we thought that special experiments should be tried in this direction in view of the strong tendency to form addition-compounds shown by the chlortrianilinodinitrobenzol. Accordingly, some of it was dissolved in anhydrous benzol and treated with dry hydrochloric acid gas. A red precipitate was formed, but this was proved by analysis to be the compound with benzol.

I. 0.3445 gram air-dried substance, when heated to 100°, lost 0.0502 gram.

II. 0.1772 gram substance gave, by the Carius method, 0.0468 gram AgBr.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_3C_6H_6$.	Found. I.	II.
C_6H_6	14.09	14.57	....
Cl	6.41	....	6.53

In a second experiment some chlortrianilinodinitrobenzol was dissolved in acetone and mixed with strong hydrochloric acid (the laboratory reagent). A dark-red precipitate was formed, which, however, was nothing but the chlortrianilinodinitrobenzol, as it melted at 179° and lost nothing when heated for some time to 130°.

Constitution of Chlortrianilinodinitrobenzol.—Judging from analogy, there can be little doubt that the atom of chlorine in the chlortrianilinodinitrobenzol stands in the meta position to the two nitro groups, but in order to place our knowledge of the structure on an experimental basis we made the chlortribromdinitrobenzol, $Br_3$1,3,5.Cl6.$(NO_2)_2$2,4, and converted this into a chlortrianilinodinitrobenzol, which proved to be indentical with the one from the tetrachlordinitrobenzol, showing that its constitution is $(C_6H_5NH)_3$1,3,5.Cl6.$(NO_2)_2$2,4.

The tribromaniline used by us was prepared in the usual way[1] by passing a stream of air saturated with bromine vapor through a dilute solution of chloride of aniline. The precipitate of tribromaniline was washed with water and used without further purification. An analysis showed that it was pure. The tribromchlorbenzol was prepared from it by Sandmeyer's reaction, as this seemed more convenient than the method of preparation of Langer[2] or Silberstein.[3] Ten grams of tribromaniline were mixed with 70 cc. of strong hydrochloric acid, and then 6.3 grams of sodic nitrite were added in small portions at a time, the flask being immersed in cold water. The dark-brown diazo solution was then treated with 12 grams of cuprous chloride, and, after the effervescence had ceased, the mixture was heated for two or three minutes on the steam-bath. After it had cooled, the gray precipitate was dried on a porous plate and was pure enough for our purpose without further treatment. In this way 9 grams of tribromchlorbenzol were obtained from 10 grams of tribromaniline, a yield of 85 per cent. The tribromchlorbenzol prepared in this way melted at 90° to 91°, that is nearly 10° higher than the melting-points ascribed to it by Silberstein, 80°, or Langer, 82°. This difference seems to be due to an obstinately adhering impurity in the product prepared by the older methods of applying the diazo reaction, for a product made by the action of hydrochloric acid on the diazo salt in acetic acid[4] melted as low as 65°, and was raised even to 82° only by long-continued

[1] This JOURNAL, **21**, 518 (1899).
[2] Ann. Chem. (Liebig), **215**, 113 (1882).
[3] J. prakt. Chem., [2], **27**, 115 (1883).
[4] Jackson and Calvert: This JOURNAL, **18**, 309 (1896).

recrystallization. That our product melting at 90° to 91° was pure is shown by the following analysis:

0.1871 gram substance gave, by the Carius method, 0.3760 gram mixture AgCl and AgBr.

	Calculated for $C_6H_2Br_3Cl$.	Found.
Br	78.79	78.18

There can be no doubt, therefore, that the true melting-point of the tribromchlorbenzol is 90° to 91°.

To prepare the tribromchlordinitrobenzol, 7 grams of the tribromchlorbenzol were boiled for half an hour with a mixture of 70 cc. of fuming nitric acid of sp. gr. 1.4 and 28 cc. of sulphuric acid of sp. gr. 1.84 in an Erlenmeyer flask, loosely closed with a glass bulb. The tribromchlorbenzol melted to a brown oil at first, and after boiling for about five minutes the tribromchlordinitrobenzol began to separate in crystals. After the liquid had cooled the substance was filtered out through glass wool and purified by crystallization from glacial acetic acid until it showed the constant melting-point 208°, when it was dried at 100° and analyzed with the following result:

I. 0.1549 gram substance gave, by the Carius method, 0.2505 gram AgCl + AgBr.

II. 0.3311 gram substance gave 19.0 cc. moist N_2 at 23°.5 and 768 mm.

	Calculated for $C_6Br_3Cl(NO_2)_2$.	Found. I.	Found. II.
Br + Cl	62.66	62.96	....
N	6.37	....	6.52

Properties of Tribromchlordinitrobenzol, $Br_3I,3,5.Cl_6.(NO_2)_2 2,4$.—It crystallizes from benzol in white, square-ended prisms usually so short that they look like cubes, from glacial acetic acid in irregular rhombic forms, resembling those of the tetrachlordinitrobenzol. It melts at 208°, and is freely soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; slightly soluble in cold glacial acetic acid, freely soluble in it when hot; essentially insoluble in cold alcohol or ligroin, slightly soluble when hot; in-

soluble in water. The best solvent for it is glacial acetic acid. The three strong acids do not affect it, nor does sodic hydrate in aqueous solution. It is decomposed with great difficulty, even by fuming nitric acid at high temperatures, and can be boiled for some time with but slight decomposition. Its properties, therefore, resemble most closely those of the tetrachlordinitrobenzol.

One gram of the tribromchlordinitrobenzol was mixed with 10 grams of freshly distilled aniline. It only dissolved partially in the cold, but on heating on the steam-bath solution took place, and the liquid became dark-red. After the heating had been continued for three hours the excess of aniline was removed with dilute hydrochloric acid and the thoroughly washed precipitate crystallized from a mixture of ligroin and benzol, until it showed a constant melting-point. As this lay at 179°, it was evident that the product was the same chlortrianilinodinitrobenzol as that made from tetrachlordinitrobenzol. For greater safety the substance was analyzed.

0.2008 gram substance gave, by the Carius method, 0.0606 gram AgCl.

	Calculated for $C_6(C_6H_5NH)_3Cl(NO_2)_2$.	Found.
Cl	7.46	7.46

Before carrying out this method of proving the structure of the chlortrianilinodinitrobenzol we tried to reach the same end by converting it into the trianilinodiaminobenzol and comparing this with a preparation of known structure, but the difficulty of handling the trianilinodiaminobenzol caused us to abandon this method for the easier one just described.

Action of Sodic Ethylate in the Cold on Tetrachlordinitrobenzol.

Ten grams of the tetrachlordinitrobenzol were dissolved in 20 cc. of anhydrous benzol and mixed with the solution of sodic ethylate prepared by treating 3.17 grams of sodium with 80 cc. of absolute alcohol, that is a little more than 4 molecules of ethylate to each molecule of the dinitro compound. The mixture was kept cold by immersing the flask in ice during the first part of the operation, as it was found the reaction

was accompanied with a considerable rise of temperature. As soon as the ethylate was added an orange-red color appeared, and a white precipitate of sodic chloride and nitrite began to form. After fifteen minutes the reaction seemed to have come to an end, as no more of the precipitate was formed, and there was no further perceptible rise in temperature, but in order to made sure that it was complete the mixture was allowed to stand in a corked flask at ordinary temperatures for two days. The liquid was then allowed to evaporate spontaneously, and the orange-red residue treated with cold water, which gave a deep red solution, and left behind a light-red, pasty mass. The latter was filtered out, washed thoroughly with water, and recrystallized from alcohol until it showed the constant melting-point 76°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.2065 gram substance gave, by the Carius method, 0.0925 gram AgCl.

II. 0.2005 gram substance gave 0.0883 gram AgCl.

III. 0.3047 gram substance gave 23.4 cc. moist N_2 at 24°.5 and 7.64 mm.

	Calculated for $C_6(C_2H_5O)_3Cl(NO_2)_2$.	Found. I.	II.	III.
Cl	10.61	11.08	10.88	....
N	8.37	....	....	8.64

The substance therefore was formed by the replacement of three of the atoms of chlorine by three ethoxy groups, judging from the structure of the trianilino body, is undoubtedly chlordinitrophloroglucine triethyl ether.

Properties of the Chlordinitrophloroglucine Triethyl Ether.— It crystallizes from alcohol in long, flat, white needles, usually terminated by one plane at an oblique angle to the sides, rarely by two planes. These crystals show a tendency to unite in parallel groups; radiating groups were not observed. It gradually turns dark on exposure to sunlight. It melts at 76° and is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold alcohol, freely soluble in it when hot; essentially insoluble in cold ligroin, moderately soluble in it when hot; essen-

tially insoluble in cold water; slightly soluble in hot water. Boiling sulphuric acid of sp. gr. 1.44 has little action on it, but a boiling dilute solution of sodic hydrate saponifies it, giving an orange-red solution, from which hydrochloric acid throws down a yellow phenol.

The dark-red, aqueous filtrate, which had been separated from the crude chlordinitrophloroglucine triethyl ether, was acidified with hydrochloric acid, and the yellow, oily precipitate thus obtained was allowed to stand for a day or two on filter-paper, which absorbed most of the oil. We can give no account of the nature of the oil extracted afterward from the paper. The more solid product could now be crystallized from ligroin, and after repeating this crystallization several times the purification was finished by recrystallization from a mixture of alcohol and water until it showed the constant melting-point 102° to 103°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.1551 gram substance gave, by the Carius method, 0.0767 gram AgCl.

II. 0.1661 gram substance gave 14.0 cc. moist N_1 at 25° and 759 mm.

	Calculated for $C_6(C_2H_5O)_2OHCl(NO_2)_2$.	Found. I.	Found. II.
Cl	11.58	12.25	....
N	9.14	....	9.34

The substance is therefore the diethyl ether, formed probably by partial saponification of the chlordinitrophloroglucine triethyl ether.

Properties of Chlordinitrophloroglucine Diethyl Ether, $C_6(C_2H_5O)_2OHCl(NO_2)_2$.—It crystallizes from dilute alcohol in slender, yellow needles with very long, pointed ends; they are often somewhat branched. It melts at 102° to 103°, and is freely soluble in alcohol, ether, benzol, acetone, chloroform, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroin, easily soluble in hot; essentially insoluble in cold water, only slightly soluble in it when hot. It dissolves in sodic hydrate, giving an orange solution of the sodium salt. The ammonium salt, made by dissolving the

ether in an excess of ammonic hydrate and warming gently till free from ammonia, gave the following precipitates:

Baric chloride, a yellow precipitate;
Plumbic acetate, an orange precipitate;
Ferric chloride, a white precipitate.

No precipitates were obtained with argentic nitrate or cupric sulphate.

Barium Salt of the Chlordinitrophloroglucine Diethyl Ether, $[C_6(C_2H_5O)_2Cl(NO_2)_2O]_2Ba$.—The salt was made by adding baric chloride to the ammonium salt of the diethyl ether. It was purified by washing with water, dried at 120° and analyzed with the following result:

0.1781 gram salt gave, by evaporation with sulphuric acid, 0.0543 gram $BaSO_4$.

	Calculated for $[C_6(C_2H_5O)_2Cl(NO_2)_2O]_2Ba$.	Found.
Ba	18.31	17.93

Properties of the Barium Salt.—It crystallized from water in small, light-yellow needles, which probably contain water of crystallization, as they turn to a dark-yellow color in a desiccator, or when heated. It is essentially insoluble in cold water; moderately soluble in hot; insoluble in cold alcohol, only slightly soluble in hot; insoluble in the other organic solvents.

Action of Hot Sodic Ethylate on Tetrachlordinitrobenzol.

Ten grams of tetrachlordinitrobenzol, dissolved in benzol, were treated with a solution of sodic ethylate made from 3.17 grams of sodium and 55 cc. of absolute alcohol, that is about 4 molecules of ethylate to each molecule of the dinitro compound, but the solution of ethylate contained less alcohol than in the previous experiments in the cold. The liquid turned orange-red immediately, and deposited a white precipitate of sodic nitrite and chloride. The temperature also rose as much as 25°, whereas the corresponding work[1] with tetrabromdinitrobenzol no evolution of heat was observed. After the addition of the ethylate the mixture was boiled for ten minutes in

[1] This JOURNAL, 18, 311 (1896).

a flask with a return-condenser. The solvents were then allowed to evaporate spontaneously, and the orange-red solid treated with water, which separated it into a dark-red solution and a pasty solid. The solution, on acidification with hydrochloric acid, gave a much more oily precipitate than that from the process carried on in the cold. As it could not be crystallized directly, it was treated with ammonic hydrate, and, after the excess of ammonia had been driven off, precipitated with baric chloride. The washed barium salt, on decomposition with dilute hydrochloric acid, yielded a yellow phenol, easily purified by crystallization from either ligroin or dilute alcohol. As it showed the constant melting-point 102° to 103°, it was the chlordinitrophloroglucine diethyl ether,

$$C_6(C_2H_5O)_2OHCl(NO_2)_2,$$

just described.

The substance insoluble in water, remaining after the sodium salt of the diethyl ether had been filtered off, was so oily that it could not be recrystallized. We accordingly distilled it with steam, when a light-yellow oil passed over, which was separated from the water and boiled for three hours with an alcoholic solution of potassic hydrate, as previous experiments had shown us that good results were obtained in this way. The dark-red solution formed deposited, on cooling, a mass of reddish crystals, the quantity of which was much increased by the addition of a large amount of water. The product thus obtained was purified by crystallization from alcohol until it showed the constant melting-point 73°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.1806 gram substance gave, on combustion, 0.2632 gram CO_2 and 0.0618 gram H_2O.

II. 0.1814 gram substance gave, by the Carius method, 0.3433 gram AgCl.

III. 0.1480 gram substance gave 0.2804 gram AgCl.

	Calculated for $C_6Cl_4(C_2H_5O)_2$.	Found. I.	II.	III.
C	39.47	39.75	....	....
H	3.29	3.83	....	....
Cl	46.71	....	46.80	46.85

The substance is therefore the tetrachlorresorcine diethyl ether formed by the replacement of the two nitro by two ethoxy groups.

Properties of Tetrachlorresorcine Diethyl Ether, $C_6Cl_4(C_2H_5O)_2$.—It crystallizes from alcohol in very slender, pointed, white needles in thick masses, the needles lying nearly, but not quite, parallel to each other. It melts at 73°, and is freely soluble in ether, benzol, chloroform, ligroin, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold alcohol, freely soluble in it hot; insoluble in water. It is not affected, apparently, by the three strong acids, or sodic hydrate.

On evaporating the filtrate from the crude tetrachlorresorcine diethyl ether a small quantity of yellow needles was obtained, which exploded on heating. On acidification they yielded the chlordinitrophloroglucine diethyl ether recognized by the constant melting-point 102° to 103°, and were therefore its potassium salt.

The quantities used in these experiments with sodic ethylate, whether hot or cold, were too small to allow the isolation of all the products of the reaction. The substances described are only the compounds, which are formed in the largest amount.

Action of Sodic Malonic Ester on Tetrachlordinitrobenzol.

Trichlordinitrophenylmalonic Ester, $C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2$.—Five grams of tetrachlordinitrobenzol were dissolved in 10 cc. of anhydrous benzol and mixed with the sodic malonic ester prepared from 5.1 grams of malonic ester and the sodic ethylate from 0.71 gram of sodium and 28 cc. of absolute alcohol. The mixture took on at once a dark-reddish color and a white precipitate began to form, but there was no perceptible evolution of heat, whereas the mixture of sodic malonic ester and tetrabromdinitrobenzol became so hot that it could not be comfortably held in the hand.[1] The mixture was allowed to stand for twenty-four hours at ordinary temperatures in a corked flask and then poured into

[1] This JOURNAL, 12, 296 (1890).

five times its volume of water acidified with dilute sulphuric acid. The yellow oil precipitated was separated from the water and the benzol allowed to evaporate spontaneously. The oily residue was dissolved in a little hot alcohol, which, on cooling, deposited an oil, but in the course of an hour this partially acidified in small, white crystals, which were washed with cold alcohol till free from adhering oil, and then recrystallized from hot alcohol until they showed the constant melting point 82°, when they were dried *in vacuo* and analyzed with the following results:

I. 0.1770 gram substance gave, on combustion, 0.2368 gram CO_2 and 0.0503 gram H_2O.

II. 0.1607 gram substance gave, by the Carius method, 9.1608 gram AgCl.

	Calculated for $C_6Cl_3(NO_2)_2CH(COOC_2H_5)_2$.	Found. I.	II.
C	36.32	36.49	....
H	2.56	3.18	....
Cl	24.74	....	24.75

The substance is therefore the trichlordinitrophenylmalonic ester.

Properties of Trichlordinitrophenylmalonic Ester.—It crystallizes from alcohol in well developed, white, short, stout prisms terminated either by one plane at a somewhat oblique angle, or by two making an obtuse angle with each other, but these principal planes are modified by many smaller planes. It melts at 82°. One one occasion the melting-point of a sample was found to be 85° to 86°, but after one recrystallization the usual melting-point 82°, was obtained, and we have not succeeded in obtaining again a substance with this higher melting-point. This observation may indicate that the substance occurs in two modifications like those of the trinitrophenylmalonic ester observed by Phinney and one of us,[1] but this influence cannot be accepted without confirmation by further experiment, which we are unable to give. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold

[1] This JOURNAL, 21, 418 (1899).

ethyl or methyl alcohol, freely soluble in either of these solvents, when hot; essentially insoluble in cold ligroin, soluble in hot; insoluble in water. Cold hydrochloric acid or cold nitric acid does not dissolve it, but hot nitric acid dissolves it, and so does cold sulphuric acid. Sodic hydrate in aqueous or even in alcoholic solution has little action on it, giving only a slight red color, and not dissolving it. This behavior is entirely different from that of the other substituted phenylmalonic esters studied in this laboratory, which give red solutions of their salts even with aqueous sodic hydrate.

Trichlordinitrophenylacetic Ester,[1] $C_6Cl_3(NO_2)_2CH_2COOC_2H_5$. — The yield of trichlordinitrophenylmalonic ester by the process described in the preceding section was very small, only 0.5 grams from 5 grams of the tetrachlordinitrobenzol. The reason was obviously that most of the substance remained dissolved in the excess of malonic ester (and perhaps also in the oily secondary products of the reaction), and was taken up by the alcohol used in treating the crude product. In order to obtain this part of the ester, the oil obtained from the evaporation of the alcohol washings was distilled with steam, and, when no more malonic ester passed over, the contents of the flask were allowed to cool and then poured into a large quantity of water. The precipitated oil, after being stirred for some time, solidified into a light-brown cake, which, on crystallization from alcohol, gave small white needles. These were recrystallized from alcohol until they showed the constant melting-point 87° to 88°, when they were dried *in vacuo* and analyzed with the following results:

I. 0.1968 gram substance gave, on combustion, 0.2437 gram CO_2 and 0.0411 gram H_2O.

II. 0.1736 gram substance gave, by the Carius method, 0.2091 gram AgCl.

	Calculated for $C_6Cl_3(NO_2)_2CH_2COOC_2H_5$.	Found. I.	Found. II.
C	33.58	33.76	....
H	1.96	2.33	....
Cl	29.80	....	29.79

[1] The nature of this body and its derivatives has not been determined with certainty. See the introduction to this paper.

The substance is therefore the trichlordinitrophenylacetic ester, but we are unable to determine whether it was formed during the action of the sodic malonic ester or the tetrachlordinitrobenzol, or, what seems more probable, during the distillation with steam by the partial saponification of the malonic ester, followed by the escape of carbonic dioxide.

Three grams of the trichlordinitrophenylacetic ester and 0.5 gram of trichlordinitrophenylmalonic ester were obtained from 5 grams of tetrachlordinitrobenzol, so that the yield was good.

Properties of Trichlordinitrophenylacetic Ester.—It crystallizes from alcohol in long, slender, branching, white needles with sharp ends, and melts at 87° to 88°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold alcohol or ligroin, freely soluble in these solvents when hot; insoluble in water. Strong hydrochloric acid or strong nitric acid has no action on it, strong sulphuric acid dissolves it. Boiling dilute sulphuric acid saponifies it, giving trichlordinitrophenylacetic acid. It is decomposed with great difficulty by fuming nitric acid. Sodic hydrate has no apparent action on it.

Trichlordinitrophenylacetic Acid, $C_6Cl_3(NO_2)_2CH_2COOH$.—This acid was formed by the saponification of its ester. One gram of the trichlordinitrophenylacetic ester was boiled in a flask with a return-condenser with about 200 cc. of sulphuric acid of sp. gr. 1.44. This large proportion of the dilute sulphuric acid is necessary to ensure complete saponification. At first the substance melted and floated on the surface of the boiling acid, then a slight yellow color was developed, and after half an hour an effervescence began, which lasted thirty to forty minutes. After two hours the oily drops had disappeared, and small white needles began to crystallize out. The liquid was then allowed to cool, diluted with about three times its volume of cold water, the white crystals formed filtered out, and recrystallized from a mixture of benzol and ligroin until they showed the constant melting-point 190° to 191°, when they were dried at 100° and analyzed with the following results:

I. 0.1796 gram substance gave, by the Carius method, 0.2346 gram AgCl.

II. 0.2264 gram substance gave 17.4 cc. N_2 at 28° and 768 mm.

	Calculated for $C_6Cl_3(NO_2)_2CH_2COOH$.	Found. I.	Found. II.
Cl	32.42	32.29	....
N	8.52	....	8.52

The yield was practically quantitative, and we are therefore unable to account for the effervescence observed during the saponification, which, at the time, we supposed was caused by the formation of a substituted toluol with the escape of carbonic dioxide.

Properties of the Trichlordinitrophenylacetic Acid.—It crystallizes from benzol and ligroin in white, well-formed prisms, probably belonging to the monoclinic system, which are usually broader than they are long, and terminated by a single plane at a very oblique angle to the sides. It was also obtained in long, slender prisms with blunt ends; and from benzol alone it crystallizes in rhombic plates, which probably contain benzol of crystallization, as they effloresce on exposure to the air. It melts at 190° to 191°, and is freely soluble in ethyl or methyl alcohol, ether, chloroform, or acetone; somewhat soluble in cold benzol, freely in hot; slightly soluble in carbonic disulphide; essentially insoluble in cold ligroin, soluble in it when hot; insoluble, or nearly so, in cold water, slightly soluble in hot. The three strong acids do not dissolve it when cold, but it dissolves in each when hot, more freely in nitric acid than in the other two. Warm sodic hydrate dissolves it, giving a yellow solution of the salt, but it is essentially insoluble in cold sodic hydrate. Even long boiling with alcohol did not convert it apparently either into the ester or the substituted toluol.

A yellow solution of the ammonium salt, prepared by dissolving the acid in warm ammonic hydrate and driving off the excess of ammonia on the water-bath, gave the following reactions:

Ferric chloride, a light-yellow precipitate;
Plumbic acetate, a yellow precipitate;
Argentic nitrate, a yellow precipitate.

With cupric sulphate there is no visible reaction at first, but after standing a few minutes light-blue needles crystallize out. Cobaltous nitrate behaves in the same way except that the needles are pink; whereas, nickelous nitrate gives no crystals even after standing fifteen minutes. Baric chloride gives no precipitate.

The silver salt was studied more carefully. It is pale-yellow and insoluble in cold water. Hot water dissolves a little of the salt, which decomposes on boiling, giving a dark-colored solution. The air-dried salt, on the other hand, can be dried at 100° without visible decomposition. It is insoluble in all the organic solvents except acetone, which gives a yellowish-brown solution with it that turns black on boiling.

CAMBRIDGE, MASS., October, 1903.

Contributions from the Chemical Laboratory of Harvard College.

THE ANALYSIS OF ORGANIC SUBSTANCES WITH THE HELP OF SODIUM PEROXIDE.

BY HANS H. PRINGSHEIM.

In a preliminary paper[1] I described a method for the quantitative determination of chlorine, bromine, and iodine as found in organic substances. In that article I promised to extend my experiments for halogen determination to a greater number of substances, and to find out whether the same method of combustion could be used for the quantitative determination of nitrogen.

I propose, in the present paper, to report upon all the experiments up to date, as now the method for halogen determination has been fully worked out.

A short time ago M. Dietrich[2] reviewed the more recent attempts to supersede the method of Carius and especially those intended to establish a new one dispensing with the use of a bomb-tube. I have solved this problem with the help of

[1] Ber. d. chem. Ges., **36**, 4244 (1903).
[2] *Ibid.*, **36**, 3385-3387 (1903).

sodium peroxide. The proposed method has all the advantages necessary for an analytical method, as accuracy, general applicability, quickness, cheapness, and cleanliness.

Parr[1] shows that coal can be completely burned by first mixing it with sixteen to eighteen times its weight of sodium peroxide, and then starting the reaction by throwing a red-hot iron wire into the mixture.

For organic compounds, which contain different percentages of carbon and hydrogen, it is necessary to fix the proportion between the substance and the sodium peroxide so that, on the one hand, the violence of the reaction may be moderated, and, on the other hand, complete combustion may be effected. This result is reached when the heat evolved is strong enough to cause such a reaction through the whole mass that the reaction-residue will be completely melted. After experiments, therefore, I fixed the proportion between different substances and sodium peroxide as follows:

Substances with 75 per cent carbon and hydrogen need eighteen times their weight of sodium peroxide; those having from 50 to 75 per cent carbon and hydrogen need sixteen times their weight of the peroxide. Substances containing 25 to 50 per cent carbon and hydrogen should be mixed with half their weight of a substance containing much carbon and hydrogen, such as sugar, naphthalene, cinnamic acid, etc.; those with less than 25 per cent carbon and hydrogen should be mixed with their own weight of one of the substances above mentioned. To the mixture is then added, in the first case, sixteen times, in the second case, eighteen times its own weight of sodium peroxide.

In most cases, however, the work can be simplified and the weighing limited to the weighing of the substance only, if we take a greater amount of sodium peroxide than the experiment calls for (approximately twice the amount) and add to it the twenty-fifth part of its weight of carbohydrate. This mixture can be made up once for all; the quantity of it to be used can be easily determined by filling the crucible up to a certain mark. This holds, when the substance does not come near to being all halogen or hydrocarbon.

[1] J. Am. Chem. Soc., **22**, 646.

Determination of Chlorine, Bromine, and Iodine in Solids.

The weighed substance, about 0.2 gram, is mixed with sodium peroxide in a steel crucible, of the form and size indicated in the accompanying illustration. The crucible is placed in a porcelain dish, in which it is surrounded with water up to the marks, which appear in the illustration near to the lid. The combustion is then started by thrusting a red-hot iron wire into the mass through the hole in the lid. After allowing it to cool for a few minutes, the crucible is laid on its side in the water and the dish quickly covered with a watch-glass. The dish is then placed on the water-bath till the mass has completely dissolved, which result will have been reached when no more oxygen is given off. The crucible and lid are then removed, washed, and the alkaline solution and wash-water filtered to remove any traces of carbon left from the combustion and any iron hydrate, which may appear in consequence of an oxidation of the wire or crucible.

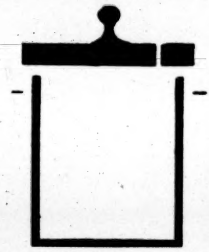


Fig. 1.

In my previous paper I proposed to pour the filtrate into so much sulphurous acid that the alkali would be completely neutralized, and still enough sulphurous acid be left to reduce any halogen acids, or peracids, formed through too strong an oxidation, to hydroacids. This same end can, however, be reached, and the bulk of the liquid considerably reduced by adding to the filtrate about 5 cc. of a strong solution of sodium sulphite and acidifying with sulphuric acid. The sulphurous acid is thus freed, particularly on gently warming. To the solution is then added strong nitric acid and the halogen is precipitated with silver nitrate. The nitric acid keeps any silver sulphite, or sulphate, in solution. After standing on the water-bath till the precipitate has settled, the silver halide is filtered, best in a Gooch crucible over asbestos, and weighed in the usual way.

Iodoform, CHI_3.—0.1345 gram substance gave 0.2407 gram AgI.

Calculated.	Found.
96.62	96.69

p-Dibrombenzene, $C_6H_4Br_2$.—0.4875 gram substance gave 0.7779 gram AgBr.

Calculated.	Found.
67.79	67.90

Dibromsuccinic Acid, $C_4H_4O_4Br_2$.—0.3479 gram substance gave 0.4740 gram AgBr.

Calculated.	Found.
57.97	57.98

2,6-Dibrom-p-nitraniline, $C_6H_4O_2N_2Br_2$.—0.1072 gram substance gave 0.1355 gram AgBr.

Calculated.	Found.
54.05	53.79

p-Chlorpropanil, $C_9H_{10}ONCl$.—0.1931 gram substance gave 0.1512 gram AgCl.

Calculated.	Found.
19.35	19.36

Chloranil, $C_6O_2Cl_4$.—0.1136 gram substance gave 0.2645 gram AgCl.

Calculated.	Found.
57.73	57.57

Diethyl Dichlordinitrophenylmalonate, $C_{13}H_{12}O_8N_2Cl_2$.—0.2114 gram substance gave 0.1535 gram AgCl.

Calculated.	Found.
17.98	17.96

Tribromresorcinol, $C_6H_3O_2Br_3$.—0.2527 gram substance gave 0.4142 gram AgBr.

Calculated.	Found.
69.16	69.76

Dinitrobrombenzoic Acid, $C_7H_3O_6N_2Br$.—0.3962 gram substance gave 0.2585 gram AgBr.

Calculated.	Found.
27.49	27.76

Eosin, $C_{20}H_8O_5Br_4$.—0.2234 gram substance gave 0.2596 gram AgBr.

Calculated.	Found.
49.38	49.44

Tetrabrom-o-quinone, $C_6O_2Br_4$.—0.4147 gram substance gave 0.7368 gram AgBr.

Calculated.	Found.
75.46	75.61

Tetrabrompyrocatechin, $C_6H_2O_2Br_4$.—0.1301 gram substance gave 0.2305 gram AgBr.

Calculated.	Found.
75.12	75.39

Hexabromphenanthrene, $C_{14}H_4Br_6$.—0.0620 gram substance gave 0.1071 gram AgBr.

Calculated.	Found.
73.62	73.52

It will be seen from the foregoing list of results that, along with other substances, I have selected a number which are particularly hard to decompose in the bomb-tube.

Since all the compounds analyzed, which contain widely different groups and belong to the aliphatic as well as to the aromatic series, have given satisfactory results, I consider the method to be generally applicable.

Determination of Chlorine, Bromine, and Iodine in Liquids.

On attempting to use the same method for liquid as for solid substances, no correct results could be obtained at first. It was found that as an average of a considerable number of determinations, about one-sixth of the halogen was lost; the higher, or lower, boiling-point of the liquid had no marked influence on the result.

That a difference exists in the oxidizing power of sodium peroxide towards solids and liquids in an open crucible was finally proven in the following way:

p-Bromtoluene, melting at 28° C., was twice oxidized. The first time the temperature, up to the time of combustion, was kept just below its melting-point, with the following result:

p-Bromtoluene, C_7H_7Br.—0.3090 gram substance gave 0.3386 gram AgBr.

Calculated.	Found.
46.78	46.63

The second time, the temperature was kept just above the melting-point up to the time of combustion, with the following result:

0.3391 gram substance gave 0.3648 gram AgBr.

Calculated.	Found.
46.78	45.78

Since in both cases the substance was weighed as a solid, the loss in the second determination must be explained as due to incomplete oxidation of the liquid.

I then tried to cover the mixture of liquid and sodium peroxide with a layer containing only sodium peroxide and carbohydrate. But this did not improve the result, as, naturally, the top layer lost its oxidizing power before the liquid was reached.

To overcome the difficulty a closed crucible, of the form and size represented in the accompanying illustration, was constructed. The lid can be screwed on. It bears in its middle a perforation just big enough to hold a capillary glass tube, into which is melted a copper wire of suitable length, ending in its lower part in a loop. The glass tube is cemented into the lid with "de Khotinski cement." Under the lid is placed a ring of softer metal, large enough to stay in its place and to rest on the rim of the crucible. This will insure, on screwing, a tighter connection.

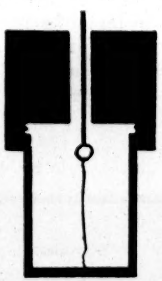


Fig. II.

Lead is too easily oxidized, but copper will serve the purpose sufficiently well. To the loop of the copper wire is fixed a

piece of fine picture wire, just long enough to touch the bottom of the crucible.

The amount of sodium peroxide demanded by the rule previously given, is now placed in the crucible. On it is poured the liquid to be analyzed, from a weighed pycnometer, which is protected against evaporation by pushing a ground glass cap over the side-tube, through which the liquid has to be poured. Ten drops of liquid will be about the desired weight. The substance and sodium peroxide are then quickly mixed with the help of a platinum wire, and the upper space in the crucible is filled with the sodium peroxide-carbohydrate mixture. The lid is screwed on, care being taken to run the fine wire through the middle of the crucible, so that it will touch the bottom.

If now the crucible is brought into connection with one pole of an electric battery, while the copper wire in the lid is connected with the other pole, the picture wire can be easily fused and the mass ignited inside of the closed crucible. If care is taken that a fuse wire has been provided, of such a thickness that it will offer less resistance than the picture wire, the direct current for electric lights can be used with convenience for this operation. It is necessary to have the crucible completely filled with sodium peroxide without, however, pressing it in. Only in this way can complete combustion of the liquid be obtained. As the carbonic acid and water formed during the reaction will be taken up by the sodium peroxide, and as nitrogen is not present in such a quantity as to create a considerable inside pressure, there is no danger of explosion connected with this operation. After cooling, the lid can be easily removed, the reaction-residue dissolved, and the halogen determined in the way described above.

Brombenzene, C_6H_5Br.—0.4060 gram substance gave 0.4829 gram AgBr.

Calculated.	Found.
50.95	50.61

o-Chlortoluene, C_7H_7Cl.—0.1564 gram substance gave 0.1798 gram AgCl.

Calculated.	Found.
28.06	28.43

Epichlorhydrin, C_3H_5OCl.—0.2132 gram substance gave 0.3279 gram AgCl.

Calculated.	Found.
38.38	38.03

Isobutyl Bromide, C_4H_9Br.—0.1680 gram substance gave 0.2289 gram AgBr.

Calculated.	Found.
58.39	57.98

Chloral Hydrate, $C_2H_3O_2Cl_3$, could be analyzed only in the closed crucible.

0.2045 gram substance gave 0.5300 gram AgCl.

Calculated.	Found.
64.35	64.09

Determination of Phosphorus and Arsenic in Organic Substances.

Although the number of organic substances, so far prepared, containing phosphorus or arsenic has not been great, this method for their quantitative determination must be considered a valuable addition, for no short method for this purpose has been in use hitherto.

For the determination of phosphorus and arsenic it is advisable to employ a somewhat larger proportion of sodium peroxide, about half the amount more in addition to that calculated for the halogen determination. It is better to oxidize the substance in a silver crucible, so as to avoid the introduction of iron, which would complicate the final determination of phosphorus and arsenic unnecessarily. For the same reason the reaction is better started by using a copper wire.

In the case of phosphorus the alkaline solution was acidified with hydrochloric acid and, after neutralizing with ammonia, was precipitated with magnesia mixture.

Guajacophospham, $P(C_6H_3(OH)OCH_3)_3$.—0.3692 gram substance gave 0.1023 gram $Mg_2P_2O_7$.

Calculated.	Found.
7.75	7.71

Diethylphosphoric Acid, $PC_4H_{11}O_4$.—0.0766 gram substance gave 0.0561 gram $Mg_2P_2O_7$.

Calculated.	Found.
20.13	20.39

In the case of arsenic the alkaline solution was twice evaporated with nitric acid to insure a complete oxidation of the arsenious to arsenic acid. This was then precipitated, washed, and weighed, following the method of Friedheim and Michaelis.[1]

Methylarsinic Acid, $AsCO_4H_5$.—0.1650 gram substance gave 0.1826 gram $Mg_2As_2O_7$.

Calculated.	Found.
53.57	53.42

Tritolylarsine, $C_{21}H_{21}As$.—0.2711 gram substance gave 0.1234 gram $Mg_2As_2O_7$.

Calculated.	Found.
21.55	21.97

Attempt at a Quantitative Determination of Nitrogen.

I thought of using the oxidizing power of sodium peroxide for a nitrogen determination, provided the peroxide would not be decomposed by dry carbon dioxide. This was found not to be the case. The substance to be analyzed was mixed with the sodium peroxide and the mixture put into a brass retort, connected on one side with a suitable arrangement for developing carbon dioxide, and on the other side through a T-tube, with a short combustion-tube, holding two reduced copper spirals of common length. This latter tube was further connected with the pipette used for nitrogen determination. After the apparatus had been completely filled with carbon dioxide the retort was closed off from the carbon dioxide generator and the pipette, and exhausted through the T-tube, to make room for the nitrogen which was then set free in the retort by starting the combustion through outside heat. The

[1] Ztschr. anal. Chem., 34, 505.

vacuum not filled with the gases, produced in the retort, was then filled up with carbon dioxide and the gases driven over the copper spirals into the azotometer, where the volume was determined. The first spiral may be oxidized by some oxygen set free during the reaction, and the oxygen so separated from the nitrogen.

In my first experiment I found 9 per cent instead of 10.37 per cent nitrogen for acetanilide. As, on repetition, no higher results could be reached and, as the deficiency of nitrogen amounted to about 10 per cent in several cases, as, for instance, 17.5 per cent instead of 20.05 per cent for potassium ferrocyanide, 27 per cent instead of 31.82 per cent for oxamide, I finally looked for nitrous acid in the reaction-residue. By using a large amount of a substance containing a high percentage of nitrogen, nitrous acid was found to be present.

So far no way has suggested itself to me of avoiding this higher oxidation, or of reducing the sodium nitrite in a way short enough to make the method practicable.

Summing up the results, I venture to say that my method is well suited to supersede the Carius method for solids; that it is available for the determination of phosphorus and arsenic; that liquids may be analyzed in a shorter time than in a bomb-tube, and perhaps with no greater number of failures in results; and that the attempt to determine nitrogen, with the help of sodium peroxide, though unsuccessful, has been an interesting experiment, and one which encourages me to further efforts.

I wish to express my thanks to Prof. C. Loring Jackson for his kind counsels in every stage of the progress of my investigation.

CAMBRIDGE, MASS., Jan. 20, 1904.

THE COMPOSITION OF DOUBLE HALOGEN SALTS.

BY H. L. WELLS.

Fritz Ephraim,[1] from observations made on double fluorides of vanadium, and from other considerations, believes that he has discovered some laws which are applicable to double

[1] Ber. d. chem. Ges., 36, 1177, 1815, 1912.

halogen salts in general. It is his opinion that the number of molecules of positive metal halide which are capable of combining with a negative halide is greater :

1. When the atomic weight of the positive metal is smaller.
2. When the atomic weight of the negative metal is greater.
3. When the atomic weight of the halogen is smaller.

These views have been criticized by Grossmann[1] and by Pfeiffer,[2] who maintain that the laws are not applicable in a general way. I will state here that I agree with the opinions of Grossmann and Pfeiffer, and without again taking up the points discussed by these authors, will make a few additional observations.

The first rule which Ephraim gives is not a new one, as far as it refers to certain series of compounds. Wells and Foote,[3] in connection with investigations on double fluorides of zirconium, noticed a rule which includes Ephraim's and applies also to the negative end of a series of salts. Their statement was as follows : "The (alkaline) fluorides of smaller molecular weight gave types with a larger number of these molecules, while the fluorides with higher molecular weights combined with more zirconium fluoride than the others."

Ephraim presents the following formulas in support of his view.

$6NH_4F.V_2F_6$	$5NaF.V_2F_6$	$4KF.V_2F_6$
$9NH_4F.3VOF_3$	$8NaF.3VOF_3$	$7KF.3VOF_3$

Wells and Foote gave the following series :

Type.	Lithium salts.	Potassium salts. Marignac.	Caesium salts.
4 : 1	$4LiF.ZrF_4.\frac{3}{2}H_2O$	.....	.....
3 : 1	.....	$3KF.ZrF_4$	.....
2 : 1	$2LiF.ZrF_4$	$2KF.ZrF_4$	$2CsF.ZrF_4$
1 : 1	.....	$KF.ZrF_4.H_2O$	$CsF.ZrF_4.H_2O$
2 : 3	.....	.....	$2CsF.3ZrF_4.2H_2O$

Wells and Foote found, however, that this rule did not apply to the sodium and thallium double fluorides of zirconium, which are as follows :

[1] *Ibid.*, **36**, 1600, 2499.
[2] *Ibid.*, **36**, 2519.
[3] Am. J. Sci., **3**, 466 (1897).

$5NaF.2ZrF_4$ $2NaF.ZrF_4$

$3TlF.ZrF_4$ $5TlF.3ZrF_4$ $\begin{cases} TlF.ZrF_4 \\ TlF.ZrF_4.H_2O \end{cases}$

Therefore, the rule evidently has only very limited application, a point which was considered by the writer in an article[1] referred to by Ephraim, and with which, consequently, he should have been familiar.

In regard to Ephraim's second and third generalizations, it may be mentioned that the effects of varying atomic weights in connection with the more negative metal and the halogen have been carefully considered, as far as they seemed to apply to certain limited series of salts, long before the matter was taken up by Ephraim. Some remarks by Wells and Campbell[2] on this subject will be merely referred to here.

Another matter must be considered here. It is the rejection by Ephraim, without any experimental evidence, and merely because, from his point of view, they ought to be simpler, of the complicated 23 : 10 (or 7 : 3) alkaline-antimonious halides. Ephraim is here inconsistent in wishing these salts to be simpler, for he has given as an evidence of his first law a salt with exactly the same complex ratio, $7KF.3VOF_2$, which has been mentioned above. Moreover, he has overlooked the work of Wells and Foote[3] on one of these salts, $7RbCl.3SbCl_3$, where the investigators made every effort to find that the salt was a mixture. His opinion that these salts are impure 2 : 1 compounds is certainly without foundation, for $7RbCl.3SbCl_3$, at least, can be repeatedly recrystallized from hydrochloric acid solution without change in composition, whether the acid is concentrated or moderately dilute. In spite of the importance attached by Ephraim to the matter, it is certain that recrystallization from hydrochloric acid would be capable either of removing or increasing, to some extent, an impurity consisting of potassium or rubidium chloride from these double salts. Too much careful work[4] has

[1] This JOURNAL, **26**, 389 (1901).

[2] Am. J. Sci., **46**, 431 (1893).

[3] *Ibid.*, **3**, 461 (1897).

[4] Some facts given by Jordis (Ber. d. chem. Ges., **36**, 2539) indicate that he has prepared the salt $7KCl.3SbCl_3$, but apparently he considers the product a mixture.

been done on these complex salts to admit of their composition being overthrown by the expression of a preference.

SHEFFIELD SCIENTIFIC SCHOOL,
NEW HAVEN, CONN., Jan., 1904.

ON THE ACTION OF DRY HYDROCHLORIC ACID GAS DISSOLVED IN ANHYDROUS BENZENE ON DRY ZINC.

BY KAUFMAN G. FALK AND C. E. WATERS.

PART I.

BY KAUFMAN G. FALK.

In an article published in 1902,[1] Kahlenberg described a number of experiments which he claimed refuted the theory of electrolytic dissociation. Among other things, he tested the action of dry hydrochloric acid, dissolved in anhydrous benzene, on a number of metals. Zinc was most readily attacked, the evolution of hydrogen continuing until a coating of the chloride was formed. The solution of acid in benzene showed no conductivity, according to a method devised by Kahlenberg. It is evident from the description of the apparatus that moisture was not entirely excluded, as the flask containing the benzene was opened just before passing in the hydrochloric acid. Rubber stoppers were also used in several places. With the intention of using the hydrogen to reduce certain substances that are acted on by water, attempts were made by me to repeat this work. Although the gases were not dried as completely as in the work of Kahlenberg, since the tubes containing the pentoxide of phosphorus were smaller, our results were entirely different from his. One would expect that the action would be greater, with more moisture present, but it entirely ceased in a few minutes, instead of continuing for hours. A protective coating was evidently formed on the zinc, and when very small amounts of water were admitted the action began again.

These facts were incidentally mentioned at the Washington meeting of the American Chemical Society by President Remsen. Afterwards H. E. Patten, in connection with whose

[1] J. Phys. Chem., 6, 1.

paper read at that meeting a discussion was started, offered to repeat his work at this laboratory. His results and the account of further work upon the subject have been published.[1] I have repeated the experiments in the same form since the article of Patten appeared, and have obtained additional data. The fact that the protective coating stopped the action was shown by shaking the flask, which removed it in part and allowed the action to start again. This is in accordance with the statements of Patten. On admitting water, however, the layer is not dissolved, as he stated, but the acid in the presence of this water seems to be able to act through the layer which is first formed, and continues to act until a second and thicker one is produced. Patten, after his visit to Baltimore, performed an experiment that was the most careful one recorded up to date. But, as he stated, the point most open to criticism was the use of rubber connections, which should have been avoided. Under these conditions the zinc was acted on as before.

We, therefore, decided to construct an apparatus that would not be liable to adverse criticism on this account. The essential features of it were devised by Dr. Frazer. Hydrochloric acid was generated in a balloon-flask by allowing concentrated sulphuric acid to drop slowly upon ammonium chloride. It was then passed through three wash-bottles containing concentrated sulphuric acid, then into a tube 20 cm. long and 2 cm. in diameter, containing alternate layers of phosphorus pentoxide and glass wool. From this it passed through a second tube containing glass wool upon which pentoxide had been deposited by distillation in a current of dry oxygen. From the drying-tubes the gas passed into one arm of an inverted T-tube, the stem of which contained a small spiral of the same zinc wire that had been used before, and which was also used by Patten in some of his experiments. To the stem was attached a guard-tube with pentoxide and glass wool, and then two Drechsel bottles partly filled with concentrated sulphuric acid. To the other arm of the T-tube was attached the inner tube of a condenser, at the upper end of which a second

[1] J. Phys. Chem., 7, 153. See especially pages 179–189.

one was attached by fusing together the inner tubes. To the lower end of the second condenser was joined a flask resembling a distilling-flask with the side tube bent upward. The neck was made by fusing to it one side of a U-tube, with a glass stopper and side tube, such as is used in organic combustions. As air was to be admitted through this tube later, it was connected with two guard-tubes containing pentoxide. The flask was partly filled with benzene that had been shaken with sulphuric acid, washed with caustic soda, then with water, dried over calcium chloride, then frozen, the last portions being discarded, and allowed to stand over phosphorus pentoxide.

Two platinum plates were fused into the side of the tube containing the zinc by means of wires, the outer ends of which were joined to short pieces of tubing that acted as mercury cups for making electrical connection. The plates were about 1 x 3 cm. and were about 1 mm. apart, and were kept in position by a drop of glass at each end. They were covered with platinum black.

The only pieces of rubber in the apparatus were the stopper of the flask in which the hydrochloric acid was generated and a piece of tubing at the outer end of one of the guard-tubes containing phosphorus pentoxide.

The stoppers of the Drechsel bottles were lubricated by the mixture recommended by Travers.[1]

When everything was ready, thin slices of sodium were put into the flask containing the benzene, which was then boiled, the first condenser returning it to the flask. At the same time a slow current of air was passed through the apparatus, escaping through two different guard-tubes of phosphorus pentoxide, so as to sweep all moisture from the apparatus. The tube containing the zinc was heated in a cylindrical air-bath to 150° for six hours. After standing three days the tube and zinc were again heated for three hours in a current of air. The next day sufficient benzene to nearly fill the reaction-tube was distilled over from the flask. To prevent this being drawn back into the flask as it cooled, the stop-cock at the

[1] Study of Gases, p. 25.

upper end of the flask was opened, thus admitting air through the two guard-tubes of pentoxide. Hydrochloric acid was then passed into the benzene through the drying-train described above. Bubbles of a gas were evolved from the zinc, and continued steadily for over an hour. The bubbles of gas were very small, and the amount of gas produced was too slight to have been measured except after the lapse of a considerable time. After two hours the action had diminished considerably, while after three hours it had practically ceased. The zinc was then covered with a thin even coating of chloride.

After the action had continued for about an hour, an attempt was made to determine the conductivity by the usual Kohlrausch method. When the reaction-tube was opposed by a resistance of 45,000 ohms no minimum could be detected. Besides the hydrochloric acid in the solution there may have been some zinc chloride, so that the conductivity would have been equal to the sum of the conductivities of the acid and the chloride. This was evidently of the order of magnitude found by Kablukoff,[1] who, using platinum electrodes 5 cm. long and 1 cm. wide and 1 mm. apart, found that the solution of hydrochloric acid in benzene had a resistance of 120,000,000 ohms. In view of these facts no further attempts to measure the conductivity were made. The hydrochloric acid is evidently not ionized as in a water solution.

A certain amount of water in the benzene seems in some way to hasten the formation of the protective layer on the zinc, so that the action stops sooner than when less water is present.

PART II.

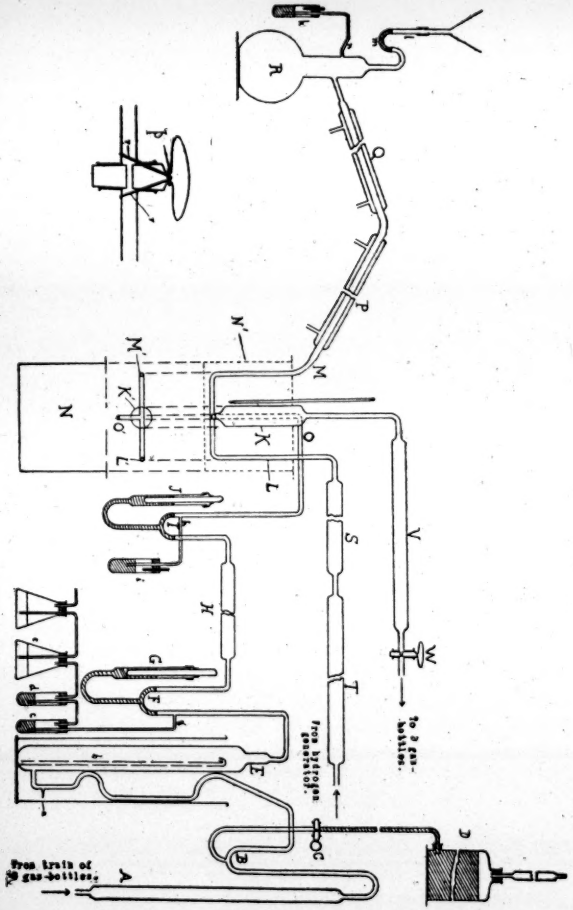
By C. E. Waters.

The results obtained by Mr. Falk appeared to be so inconclusive that it was determined to repeat his experiments, taking even greater precautions than before. The one point that seemed most open to adverse criticism was that the zinc was heated in a current of air in order to dry it. It would thus become covered with a film of oxide, which would form

[1] Ztschr. phys. Chem., 4, 429.

water if acted upon even to the slightest extent by the acid. Accordingly, a slow current of carefully dried hydrogen was used instead of air. The apparatus was practically the same as that used in the experiments described in Part I. But instead of three, there were seven wash-bottles containing concentrated sulphuric acid, and the hydrogen was purified by passing it through a solution of potassium permanganate, and then through an alkaline solution of pyrogallol. After this it went through a bottle with sulphuric acid, and then swept out the air from a flask, provided with a dropping-funnel and a delivery-tube, in which the hydrochloric acid was to be generated. From the flask it went through six wash-bottles fused together. Thence it was passed through tubes containing phosphorus pentoxide, etc., as in the experiments of Falk. The hydrogen was supplied from a Kipp apparatus provided at the top with a rubber stopper and a five-foot tube, of 1.5 cm. bore, in order to obtain the necessary pressure to force the gas through all the bottles of acid. By means of a pinch-cock the flow was so regulated that only ten or twelve bubbles passed per minute. The gas was allowed to flow all night, and the next day the tube containing the zinc was heated in the air-bath to a temperature of 300°–320° C. for eight hours. On the following morning, the benzene which had been standing over sodium, and then boiled with it as described by Falk, was distilled over into the tube containing the zinc. Then concentrated sulphuric acid was allowed to drop slowly from a long-stemmed dropping-funnel upon ammonium chloride, thus causing a slow current of hydrochloric acid to pass through the apparatus. When the benzene became well saturated with the gas there was evidently some action on the zinc, though even less than in the experiments of Falk. This continued for two or three hours, when the surface of the zinc was dark and slightly corroded. In our experiments the substances were plainly more carefuly dehydrated than before, and there was less action, so that it appeared probable that there would be none at all if all the moisture were removed.

At the suggestion of Dr. Frazer, an apparatus was con-


R
P
N'
M'
M
N
K'
K
L'
L
O
Q
S
V
W
To 2 gas-bottles.
From hydrogen generator.
T
J
H
G
F
E
D
C
B
A
From train of 10 gas-bottles.

structed in which the hydrochloric acid gas could be kept in contact with the phosphorus pentoxide as long as desired. A description of the apparatus and the method of procedure follows: Hydrochloric acid was generated in a wide-mouthed bottle by allowing concentrated sulphuric acid to drip slowly upon ammonium chloride. A three-way stop-cock was introduced into one hole of the rubber stopper in order to pass the gas through the apparatus or to reduce the pressure rapidly, if desired, without permitting any back-flow of liquid from the drying-bottles. From this bottle the gas went through three Drechsel bottles fused together and containing sulphuric acid. It then went through a tube, *A*, 800 mm. long and 20 mm. bore, containing layers of phosphorus pentoxide and glass wool. At first the gas was allowed to pass out through *D* so as to sweep out the tube above the stop-cock *C*, after which it was sent through *E*, which was filled with pentoxide and glass wool. Before being filled with the drying agents, this tube was drawn out somewhat at the top so as to admit less moisture when the small tube was finally sealed to it. The mercury trap, *F*, being closed, the gas escaped through the lateral tube, *g*, under the mercury in *c*, which contained also a little pentoxide, then into *d* with sulphuric acid, and finally into water in the flasks *e* and *f*. These were so arranged as to prevent the water from sucking back into the acid.[1] When the air was driven from *E* mercury was run into *B* from *D*, and in this way the hydrochloric acid could be kept in contact with the pentoxide as long as desired. The tube *G* was then fused off.

The mercury trap, *F*, was made without the use of a bulb and long rubber tube, so as to avoid any diffusion of moisture into the apparatus. The tube, *G*, contained a piston, the outside diameter of which was about 4 mm. less than the bore of the tube, and was held air-tight by means of a short piece of rubber tubing fitted over both glass tubes. When the piston was not in the mercury the surface of the latter was just below the curve of *F*. By pushing the piston down, and at the same time slightly loosening the rubber, the mercury

[1] Lassar-Cohn: Arbeitsmethoden, 3rd. Edition, p. 311.

could be brought to any desired level in *F*, and to the same height in *G* by simple displacement. In this way there could be no tendency for the mercury to shift its level, as was seen to be the case when it stood higher in one tube than in the other. A little pentoxide was placed on the surface of the mercury in *G*, and all the mercury that was used here and throughout the apparatus was dried by shaking with pentoxide. The trap *I* was similar to *F*.

The tube, *H*, contained phosphorus pentoxide that had been distilled in a current of dry air and deposited upon glass wool previously placed in it. It was shut off from the rest of the apparatus by the traps, *F* and *I*. Further mention will be made of it later. While the hydrochloric acid was being passed through one part of the apparatus, the air was being driven from the rest of it by means of a slow current of hydrogen from a Kipp's apparatus, as already described. From the bottles containing potassium permanganate and pyrogallol it passed through six bottles of concentrated sulphuric acid into the tube, *T*, containing phosphorus pentoxide, and then through a second one, *S*, with redistilled pentoxide. Thence it passed through *L* into *K*, *O*, or *M*, as desired. In order to lose as little time as possible in driving the air out, the current of hydrogen was started one afternoon and allowed to run slowly all night, the cock, *W*, being open. In the morning it was closed and the hydrogen sent through *M* to drive out the air from the flask and condensers, and finally through *O* and out by way of *i*. The flow through the last two tubes was regulated by means of the glass plugs in the stoppers of the tubes containing mercury. At all times the current of gas was very slow. To drive the air from *R*, the benzene was kept boiling gently, and in this way the vapors filled the tube up to *n*, and the air above it would escape by diffusing into the hydrogen. When it was safe to heat the tube, *K*, a cylindrical air-bath, *N*, sheathed with asbestos, was placed under it on a tripod. The tube was kept at a high temperature. Preliminary experiments showed that when zinc dust is dried in a current of air at 365°–398° for two hours and then heated in a current of dry hydrogen at 355°, it gives up con

siderable moisture. From this it is believed that any zinc oxide that might be on the surface of the zinc would be reduced before the hydrochloric acid and benzene came in contact with it.

Of course the benzene was introduced before the current of hydrogen was started. A funnel was attached to the end of *l* by a rubber tube, and the benzene, which had been dehydrated, as already stated, was mixed with fresh pentoxide and poured in. The bend of the tube was then washed with a little pure benzene and enough mercury to close the bend was poured in. The outer end was then dried inside with a bit of paper and the tube sealed off with a small flame. In this way no moisture was admitted from the flame, and there was no danger of an explosion from the benzene vapor and air when it was sealed off.

When the hydrochloric acid had stood long enough in contact with the pentoxide in *E*, steam was run into the jacket of *Q* and at the same time the benzene was heated to boiling by means of a hot water-bath. A little more than enough to cover the zinc was distilled over. The water-bath was then cooled somewhat, but still kept under *R* to prevent the benzene from being drawn back again into the flask. Then the cock, *C*, was opened to admit some mercury, so that the gas in *E* was under a slightly greater pressure than in the tubes *H* and *K*. The traps, *F* and *I*, were then opened by raising the pistons. More mercury was then run into *E* so as to drive the gas slowly through *H*, which contained redistilled pentoxide, into the benzene in *K*. In order to prevent any possible stoppage of the mercury, the tube, *b*, with holes every inch or two, was placed in *E*, the idea being that the mercury could find its way up through this past any obstacle. The top was bent over to prevent its being clogged with pentoxide when *E* was filled.

The results of some experiments are given :

1. Some zinc was distilled under diminished pressure in an atmosphere of dry nitrogen, practically according to the method of Morse and Burton.[1] A small rod of it was filed into

[1] This JOURNAL, **10**, 312 (1888).

shape and smoothed with sandpaper. It was placed in *K* with a spiral of the same wire that was used in the previous experiments. They were kept from touching one another by placing the rod in a bit of glass tube open at each end. The wire was evidently impure, for it was acted on readily by dilute aqueous hydrochloric acid, giving at first a considerable residue that afterward dissolved. The sulphide was of a dirty yellowish-white. The distilled zinc was made from a specimen purer at first than the wire, and it was acted on only very slowly by aqueous hydrochloric acid. The sulphide was pure white. When a piece of filter-paper moistened with silver nitrate solution was held in the escaping hydrogen it was seen that both specimens of zinc contained arsenic. The wire contained more than commercial granulated zinc, while it took several minutes for the dark spot to appear when the distilled zinc was used.

The zinc was heated to 375° for two hours, and then to 355° for three hours. The hydrochloric acid was allowed to stand in contact with the pentoxide in *E* for twenty-four hours. When it was passed into *K* a tiny leak was noticed at the end of *H* nearest *F*, but nevertheless the experiment was continued to test the apparatus. There was evidence of exceedingly slight action on the wire, and what was surprising, a little more hydrogen came from the pure zinc. It was estimated that the gas was given off as rapidly as in the last experiments of Falk, but at no time could the action be called violent or rapid. The bubbles continued to appear for perhaps an hour.

2. The apparatus was then taken apart, cleaned, dried, and reconstructed. Fresh pieces of zinc were used, and were heated for five hours to 365° to 398°. The hydrochloric acid was kept in contact with the pentoxide in *E* for twenty-four hours. By the time the presence of hydrochloric acid could be detected at *W*, which was loosened for a moment, it was seen that bubbles were being given off from the surface of the piece of redistilled zinc in *K*. They seemed to come off from definite spots, and not from the entire surface. This continued for more than an hour. At no time was there any evidence to show that the coil of impure wire was being acted

upon. Not a single bubble was seen to come from its surface. The fact that it was enclosed in a tube slightly contracted at the lower end could have nothing to do with this, for nearly every bubble of hydrochloric acid passed through the tube, and there was free circulation of the liquid in all parts of *K*.

The way in which the hydrogen came from definite spots on the pure zinc seemed to indicate impurities giving an electrical couple, perhaps iron from the file with which the stick was shaped, though the surface was afterwards cleaned with sandpaper and filter-paper wet with benzene in the same way as the wire. It may be that particles of iron lodged in the crevices between the crystals of the zinc. Another thing that may have been a disturbing factor was that part of the surface of the zinc was much darkened after the heating, and the rest of it seemed to be clouded, instead of bright. Perhaps this was due to a deposit of carbon. An acid solution of permanganate gives off oxygen slowly, and this would tend to produce carbon monoxide when it was passed into the pyrogallol. It might easily happen that the monoxide would be reduced to carbon on the surface of the zinc when heated to 398° in hydrogen. When the apparatus was taken apart for cleaning, it was noticed that the dark deposit was nearly all removed by water. The few bits that remained could be rubbed off with ease. This is what we should expect if it were a superficial deposit of carbon.

3. The experiment was again repeated, removing the oxygen this time by means of copper. Copper powder was made by sifting zinc dust into a hot solution of copper sulphate, washing the precipitated copper with alcohol, then mixing it, while still moist, with short-fibred asbestos, washing with ether, and drying in a desiccator. The material was then placed in a tube of hard glass closely wound with copper gauze to prevent its bursting, when heated red-hot, under the pressure of the hydrogen. Instead of filing down a large stick of the redistilled zinc, a clean piece of it was melted in an atmosphere of nitrogen at reduced pressure, in a piece of Jena tubing closed at the lower end and drawn out to a tube of

about 4 mm. bore. In this way a slender rod of it was obtained that could be cleaned with sandpaper. With it were introduced a piece of the same wire that was used in the previous experiments, and a second piece of the wire with a little platinum wire wrapped around the middle. These were kept from touching one another by being placed in short pieces of glass tubing. To keep the pieces of zinc from falling out of the tubes, a sort of grating was formed at the bottom of each by drawing threads of melted glass rod across the opening.

When the apparatus was set up the copper was first reduced in a current of hydrogen, the water which was formed being allowed to escape at one end of a T-tube, which was closed when it was desired to pass the hydrogen through the apparatus. It is evident that all the oyxgen, which could be present only in small amount, would be burned to water in contact with the red-hot copper and hydrogen.

After the benzene was distilled over into *K*, in this experiment, it was heated just to its boiling-point by means of the air-bath. This was done at the suggestion of Professor Morse, in order to remove the surface film of hydrogen upon the zinc.

The hydrochloric acid was kept in *E* for nine days. When it was passed into the benzene there was action on all the pieces of zinc. The rod of the distilled zinc and the wire seemed to give off equal amounts of hydrogen, while the wire with the platinum wrapped around it was apparently acted on least, though this may not have been due to its smaller surface. The action was greater than in the experiments preceding, though it was still exceedingly slow, and it ceased entirely within an hour. The zinc was slightly darkened and none of the white coating noticed by Patten was seen.

According to some rough determinations, benzene dissolves about two per cent of hydrochloric acid, by weight, at 18° C.

Various devices suggested themselves in connection with the working of the apparatus. To empty *E* with least risk, a small tube, *a*, was fused to the tube through which the mercury entered. At the proper time its point was broken off with a long rod, and the mercury flowed quietly into the cyl-

inder. In wiring in stopcocks there is no middle ground, they are either too tight or too loose. If rubber bands are simply twisted around them, the cock is apt to turn at the wrong time. Accordingly a piece of wire, *p*, was fastened to the cock so as to make a loose collar with two projecting hooks on opposite sides. The rubber band was then slipped over these hooks, and the cock could be set at any point and left without fear of its moving back. A similar device was used on the Drechsel bottles to keep the stoppers in place in spite of the pressure inside. Two strong bands were used on each bottle. The bottles were placed on little tables, made by nailing together three pieces of half-inch boards, six inches square, so that it was not necessary to cut them apart to clean and refill them. By slipping out the table the bottle could be removed from the stopper.

The admission of some moisture in sealing the joints of the apparatus is unavoidable. The amount thus introduced is lessened by keeping the ends of the tubes to be joined close together while being heated. In blowing into the apparatus to perfect the joint, a tube containing phosphorus pentoxide was always between the mouth and the apparatus.

Many useful suggestions were received from different workers in the laboratory, especially from Dr. J. C. W. Frazer.

JOHNS HOPKINS UNIV.,
December, 1903.

RECENT RESEARCH ON RADIOACTIVITY.[1]

BY P. CURIE.

Since the discovery of strongly radioactive substances, research on radioactivity has been greatly developed. I propose in this article to give an account of the actual state of our knowledge relative to this subject, laying particular stress on the most recent work.[2]

[1] Translated from an article that appeared in *Jour. d. Chim. Phys.*, **1**, 409 (1903), edited by Philippe A. Guye, Professor of Chemistry in the University of Geneva. See This JOURNAL, **31**, 298 (1904).

[2] For more complete details of work done previous to May, 1903, see the thesis of Mme. Curie. It appeared in *Ann. de Chim. et de Phys.* in 1903 and 1904.

I. Radioactive Substances.

Becquerel Rays. Uranium and Thorium.—We call radioactive such substances as are capable of emitting spontaneously and continuously certain rays known as Becquerel rays. These rays act upon the photographic plate; they render the gases through which they pass conductors of electricity; they can pass through black paper and metals. The Becquerel rays cannot be reflected, refracted or polarized.

In 1896 Becquerel discovered that uranium and its compounds emit these new rays continuously. Schmidt and Mme. Curie then found almost simultaneously that thorium compounds are also radioactive. The radiations emitted by thorium compounds are comparable in intensity with those from the compounds of uranium. Radioactivity is an atomic property that accompanies the atoms of uranium and thorium wherever they are found; in a compound or a mixture its intensity is proportional to the amount of the metal present.

New Radioactive Substances.—Mme. Curie, in 1898, tried to learn whether there were among the elements then known any others possessing radioactivity; she could not find a single substance giving any considerable radiation, and concluded that the radioactive properties of the elements are at least 100 times more feeble than those of uranium and thorium. She found, on the other hand, that certain minerals containing uranium (pitchblende, chalcolite, and carnotite) are more active than metallic uranium; the activity of these minerals could not, then, be due solely to uranium or to other known elements. This discovery was fertile with new results. Mme. Curie and I showed, in an investigation carried on together, that pitchblende contains new radioactive substances, and we supposed that these substances contained new chemical elements.

There are known with certainty three new strongly radioactive substances: polonium, which was found in the bismuth obtained from the uranium minerals; radium, found with barium from the same source, and actinium, which was dis-

covered by Debierne among the rare earths extracted from the same minerals. These three substances are present only in infinitesimal quantities in the uranium minerals, and all three possess a radioactivity about a million times greater than that of uranium or thorium.

Recently Giesel and Hofmann announced the presence of a fourth strongly radioactive substance in the uranium minerals, which had properties closely resembling those of lead; from the publications that have appeared up to this time I have not been able to form an opinion as to the nature of this substance.

It may be asked whether radioactivity is a general property of matter. This question cannot be regarded as actually settled. The investigations of Mme. Curie have proved that the different known substances do not possess an atomic radioactivity one-hundredth as great as that of uranium or thorium. On the other hand, certain chemical reactions may cause the formation of ions, conductors of electricity, without the active substance giving any evidence of atomic radioactivity. Thus white phosphorus by its oxidation renders the surrounding air a conductor of electricity, while red phosphorus and the phosphates are not at all radioactive.

Some old experiments by Russell, Colson and Lengyel showed that certain substances act upon the photographic plate at a distance. It is possible that this phenomenon is partly due to radioactivity, but it is not certain. Recent work by MacLennan and Burton, Strutt, and Lester Cooke, leads to the supposition that radioactivity belongs to all bodies to an extremely slight extent. The identity of these very feeble phenomena with atomic radioactivity can not yet be regarded as proved.

Radium.—Of all the strongly radioactive substances radium is the only one that has been proved to be a new element. Radium possesses a characteristic spectrum, the discovery and first study of which we owe to Demarçay, and which has since been studied by Runge and Precht and by Crookes. Radium is an element belonging after barium in the series of

alkaline earths. Its atomic weight as determined by Mme. Curie is 225.

At present radium is obtained from a residue left on extracting uranium from pitchblende. This residue contains 2 or 3 decigrams of radium in a ton. At first 10 or 15 kilograms of radiferous barium salt are extracted from a ton of the residue, and from this the radium is prepared by fractional crystallization (with the chloride or bromide), the crystals that form from the solution being richer in radium than the salt that remains in the liquid.

The radiant activity of the radium salt can be measured at different times from the beginning of crystallization until it is finally dried in the air-bath. It is found that the activity has a certain initial value, then it increases as a function of the time, at first rapidly, then more and more slowly; it approaches asymptotically a limiting value which is about five times as great as the initial activity. The activity then remains invariable for some years if the salt be left as it is.

Polonium.—Polonium is, on the contrary, a substance that slowly loses its radioactivity from the moment when it is separated from the uranium mineral containing it. After some years the radioactivity of polonium almost completely disappears. Hence it acts like an unstable substance. It has not yet been shown that polonium is a new element distinct from ordinary bismuth.

Polonium can be concentrated by fractionally precipitating the subnitrate of polonium and bismuth by means of water. The part precipitated is the most active. One can also make a partial precipitation by means of hydrogen sulphide from a strongly acid solution in hydrochloric acid. These methods of fractionation are difficult because the precipitates are not easily redissolved. Marckwald concentrated the activity by plunging a rod of bismuth in a solution of bismuth and polonium. A layer of extremely active metal was deposited upon the rod.

Actinium.—The concentration of actinium is even more difficult than that of polonium. Solid salts containing actinium preserve their radioactivity unchanged for several years.

II. The Radiations from Radioactive Substances.

Complexity of the Radiation.—Radium is the substance whose radioactivity has been studied most completely. It is now known that it emits a number of rays of different nature, which can be placed in three groups. According to the notation adopted by Rutherford, I designate the three groups of rays by the letters α, β, and γ.

The action of the magnetic field serves to distinguish them. In an intense magnetic field the α-rays are slightly deviated from a straight path, and the deviation is of the same kind as that of the "canal" rays of Goldstein in a vacuum-tube. On the other hand, the β-rays are deviated like the cathode rays, and the γ-rays are not turned aside, but act like the Roentgen rays.

β-Rays.—The β-rays of radium, analogous to the cathode rays, form a heterogeneous group. They are distinguished from one another by their power of penetration and by the deviation caused by a magnetic field.

Certain β-rays are absorbed by aluminium foil a few hundreths of a millimeter in thickness, while others pass through several millimeters of lead.

Suppose we have a rectilinear pencil of Becquerel rays obtained by means of a particle of radium salt and a screen with a hole in it. If a uniform magnetic field is produced normal to the direction of the pencil the β-rays are incurved, and describe circular paths in a plane normal to the direction of the magnetic field. The rays of the described circumferences vary within wide limits. Becquerel has shown that the most penetrating rays are least deviated, and hence describe circumferences with the greatest radius of curvature. If the pencil of β-rays bent aside by the magnetic field is allowed to fall on the photographic plate, there is obtained an impression that is a true spectrum in which the different β-rays act separately.

Suppose the β-rays to be projectiles (electrons) negatively charged with electricity and shot from the radium with great velocity. Let m be the mass of a projectile, e its charge, v

its initial velocity, ρ the radius of curvature of its path, H the intensity of the magnetic field normal to the initial velocity, μ the magnetic permeability of the medium. We then have the easily established relation

$$\mu H\rho = \frac{mv}{e}. \tag{1}$$

The β-rays are also deviated in an electric field. Suppose we have a rectilinear pencil of these rays. If a uniform electric field be produced normal to the initial direction of the pencil, the rays are deviated in the opposite direction to the field, and describe parabolic paths. The experiment can be performed by passing the pencil of rays between two parallel metallic plates, between which there is established a difference of potential. The deviation is slight with the means one has at command, and it is convenient to work in a vacuum. The air is made a conductor of electricity, so that if we work in the air the insulation is imperfect, and it is difficult to maintain a constant and high difference of potential between the plates. The most penetrating β-rays are bent aside least.

The action of the electric field is in accord with the ballistic hypothesis previously stated. Accepting this hypothesis, suppose a uniform electric field with an intensity h and a width L acts upon the charged projectile whose initial velocity is normal to the field. The deviation, y, of the extremity of the trajectory at the departure from the field is given by formula (2), when the deviation is slight.

$$\frac{hL^2}{2y} = \frac{mv^2}{e}. \tag{2}$$

From the equations (1) and (2) can be deduced the velocity, v, of the projectiles, and the ratio, $\frac{e}{m}$, of the electric charge to the corresponding mass.

The experiments of Becquerel have shown that for the β-rays of greatest intensity the ratio, $\frac{e}{m}$, approaches 10^7

electromagnetic units, and v a value of 1.6×10^{10} $\frac{cm}{sec}$. These values are of the same order of magnitude as for the cathode rays.

Kaufmann has made exact experiments on the same subject. This physicist subjected a very narrow pencil of radium rays to the simultaneous action of a magnetic and an electric field, both fields being uniform and acting normal to the primary direction of the pencil. The pencil is received upon a photographic plate placed perpendicular to its initial direction. In the absence of the two fields the impression on the plate is a small circular disk, almost like a point. When the magnetic field acts alone the different β-rays are unequally deflected but remain in a plane normal to the field, producing upon the plate an impression in the form of a straight line. When the electric field acts alone the different β-rays are unequally deflected in a plane passing through the field and producing upon the plate an impression which is a straight line perpendicular to the one preceding. When both fields act simultaneously the impression on the plate is a curve. Each point of the curve corresponds to a different kind of β-ray. Taking as axes of coordinates on the plate the straight lines obtained when each of the two fields acts alone, the coordinates of each point of the curve represent the relative magnetic and electric deviations for each kind of ray.

The following are the figures for v and $\frac{e}{m}$ obtained by Kaufmann, referred to the most penetrating rays of radium. I give for comparison the values obtained by Simon for the cathode rays.

$\frac{e}{m}$ in electromagnetic units.	v $\frac{cm}{sec}$.	
1.865×10^7	0.7×10^{10}	(For the cathode rays. Simon.)
1.31×10^7	2.36×10^{10}	(For the radium rays. Kaufmann.)
1.17×10^7	2.48×10^{10}	
0.97×10^7	2.59×10^{10}	
0.77×10^7	2.72×10^{10}	
0.63×10^7	2.83×10^{10}	

It is seen that certain β-rays have a velocity approaching that of light. One can understand why it is that particles having such velocity should be able to penetrate matter to such an extent, although they are so small.

The ratio $\frac{e}{m}$, seems to be the same for the least penetrating radium rays and the cathode rays. But this ratio dimishes as the velocity of the rays increases. J. J. Thomson and Townsend think that all charged electrons, when in motion, possess the same charge, which is equal to that carried by an atom of hydrogen when a solution is electrolyzed. If that be true, it must be admitted that the mass of the particles increases with their velocity, when the latter approaches that of light.

In the case of electrolysis the ratio, $\frac{e}{m}$, is equal to 9650, while this same ratio is equal to 1.865×10^7 for the cathode rays and the less penetrating β-rays. If it be admitted that the charge, e, is the same in both cases, it can be deduced that the mass of an electron is about two thousand times less than that of an atom of hydrogen.

Theoretical considerations lead to the conception that the inertia of a particle is solely due to its being a moving charge, the velocity of a moving electric charge not being altered without some change of energy. In other words, the mass of the charged particle is, in part at least, an apparent mass or an electromagnetic mass. Abraham gave a formula for calculating the electromagnetic mass of a charged particle as a function of its velocity. According to this formula the mass due to electromagnetic reactions is a constant for low velocities; it increases with the velocity, and approaches infinity for velocities that approach that of light. The experiments of Kaufmann are in accord with this theory, and also lead to the conclusion that the mass of an electron is entirely of an electromagnetic nature. These results are of great theoretical importance. One can foresee the possibility of establishing mechanics upon the dynamics of small material centers charged and in motion.

α-Rays.—The α-rays of radium have very little power of penetration. A piece of aluminium foil a few hundredths of a millimeter in thickness absorbs them almost completely. They are also absorbed by the air, and cannot penetrate air at the atmospheric pressure to a greater distance than 10 cm. The α-rays form the most important part of the radiation of radium, provided we measure the radiation by the amount of ionization which it produces in the air.

The α-rays are very slightly deflected by the most intense magnetic and electric fields, and they were at first thought to be non-deviable under this influence. Nevertheless, independently of the action of the magnetic field, the laws of the absorption of the α-rays by superimposed screens is sufficient to distinguish them clearly from the Roentgen rays. In passing through successive screens the rays become less and less penetrating, while the penetrating power of the Roentgen rays increases. The ray is like a projectile whose energy diminishes on passing through each screen. A given screen also absorbs the α-rays to a much greater extent when it is placed at a distance than when it is placed quite near the radium.

Strutt suggested that the rays might be analogous to the canal rays of vacuum-tubes. Rutherford succeeded in showing the action of a magnetic field upon the rays and in making a preliminary measurement of the deviation. Becquerel confirmed the results obtained by Rutherford and gave a new measurement of the phenomenon. Des Coudres measured the electrical and magnetic deviation of the rays in a vacuum.

From these investigations it is seen that the α-rays act like projectiles having a great velocity and charged with electricity. The deviation in a magnetic field and in an electric field is the opposite of the deviation of the cathode rays.

The α-rays form an apparently homogeneous group, all being deflected to the same extent and, hence, not giving a spread-out spectrum as the rays do. The formulas (1) and (2) are applicable. According to the measurements of des Coudres in a vacuum,

$$v = 1.65 \times 10^9 \quad \text{and} \quad \frac{e}{m} = 6400.$$

Hence the velocity of the particles is twenty times less than that of light. If we assume that the charge of a particle is the same as that of an atom of hydrogen, in electrolysis, it is found that its mass is of the same order of magnitude as the hydrogen atom (the ratio, $\frac{e}{m}$, is equal to 9650 for hydrogen in electrolysis). It may well be supposed that these particles, which are greater than the electrons and have a lower velocity, would be less capable of penetration.

According to the experiments of Becquerel, the curvature of the path of the α-rays moving in a uniform magnetic field is not constant when in air at the atmospheric pressure. At first the curvature is the same as that obtained in a vacuum, but it becomes less and less as the ray recedes from its source. This phenomenon can be explained by supposing that new particles attach themselves to the projectiles that make up the rays while the latter move through the air. This hypothesis explains why the absorbing power of a screen for the α-rays increases as it is removed farther from the radiant source.

The α-rays are the ones that are active in the very beautiful experiments with the spinthariscope of Crookes. In this apparatus a very small fragment of a salt of radium (a fraction of a milligram) is held by a metallic thread a short distance (0.5 mm.) from a phosphorescent screen of zinc sulphide. On examining, in the dark, the surface of the screen which is toward the radium by means of a magnifying glass, luminous points are seen sprinkled over the screen, reminding one of a starry sky. These luminous points appear and disappear continuously. From the ballistic theory it might be imagined that each luminous point that appeared and disappeared resulted from the shock of a projectile. This is the first instance of a phenomenon which enables one to distinguish the individual action of an atom.

γ-Rays.—The rays are exactly like the Roentgen rays. They seem to comprise but a small part of the total radiation. The γ-rays have a very extraordinary power of penetration, and they diffuse very little in passing through most substances.

Diffusion of the Radium Rays.—Suppose we have a pencil of Becquerel rays issuing from radium and limited by a screen of lead. If the pencil meets a thin screen the α-rays are absorbed, the β-rays are diffused in all directions, and the γ-rays go part way through the screen as a well-defined pencil with sharp edges. The γ-rays can also pass through a prism of thick glass as a well-defined straight pencil. The question has been raised whether the β-rays are always completely diffused when they penetrate a solid screen. The experiments of Becquerel show that a pencil of β-rays can propagate itself in a well defined way in paraffin. Becquerel made use of the action of the β-rays on the photographic plate to study the path of the rays when dispersed by a magnetic field. It can be seen from the prints that the most penetrating rays pass through 7 or 8 mm. of paraffin without marked diffusion, while the least penetrating rays are completely diffused after passing through 2 mm. The magnetic field deflects the β-rays in paraffin as in air.

Conductivity of Dielectric Liquids under the Influence of the Radium Rays.—Dielectric liquids become poor conductors under the influence of the radium rays. This can be shown with petroleum, ether, vaseline oil, benzene, amylene, carbon disulphide, and liquid air.

Radiation of Other Radioactive Substances.—Polonium emits only very slightly penetrating rays, which seem to be identical with the α-rays of radium. They possess almost the same power of penetration and are deflected in the same way by the magnetic field. Finally, the experiment of the spinthariscope can be performed with the α-rays of polonium. Hence, polonium is a source of the α-rays unmixed with other kinds of rays, which is of value in certain studies. But the source exhausts itself, and some years after it has been separated from the minerals containing it the polonium loses its activity.

Thorium, uranium, and actinium seem to emit the α- and β-rays; the deviability of the β-rays has been shown.

The Electric Charge of the Radium Rays.—According to the

ballistic theory, the α-rays should carry positive electric charges and the β-rays negative electric charges. Mme. Curie and I have shown that, in conformity to the theory, the β-rays of radium charge positively the bodies that absorb them. To show this, a plate of lead is connected with an electrometer. The plate of lead is entirely covered with a layer of paraffin, which is in turn enveloped in fine aluminium foil connected with the earth. The radium, placed in a small dish, sends its rays upon the plate of lead, which is thus protected. The α-rays are stopped by the exterior layer of aluminium. Part of the β-rays pass through the aluminium and the paraffin and are absorbed by the lead, which becomes charged negatively. The paraffin is necessary to sufficiently insulate the plate of lead, which could be charged if it were surrounded by air, for it is made a conductor by Becquerel rays.

We have also shown that a salt of radium is charged positively when it is enveloped in an insulating layer, and that it emits β-rays from the exterior, while the α-rays cannot escape.

A sealed glass bulb containing a salt of radium becomes spontaneously charged like a Leyden jar. If after a sufficient time a mark is made on the wall of the flask with a glass-cutter, a spark is discharged, which pierces the glass at the point where it was made thin by the cutter. At the same time the experimenter feels a slight shock in his fingers from the passage of the discharge.

Phosphorescence of Substances under the Action of the Becquerel Rays. Light Emitted by Salts of Radium. Coloration of Substances by the Action of the Rays.—The radiation from radium causes phosphorescence in a great many substances: the salts of the alkalies and alkaline earths, uranyl-potassium sulphate, organic substances, cotton, paper, cinchonine sulphate, skin, glass, quartz, etc. The most sensitive substances are barium platinocyanide, willemite (silicate of zinc), sulphide of zinc, and diamond. With the penetrating β-rays willemite and the platinocyanide are the most sensitive, while

with the α-rays it is better to use phosphorescent sulphide of zinc.

Phosphorescent substances are altered by the prolonged action of the radium rays. They become less excitable and are less luminous under the influence of the rays. At the same time they change their color or become colored. Glass becomes violet, black or brown. Salts of the alkalies turn yellow, green or blue. Transparent quartz becomes smoky quartz. Colorless topaz turns yellow, orange, etc. Glass colored by radium is thermoluminescent. On heating it to 500° it emits light. At the same time it becomes colorless and returns to its original condition. It is then capable of being colored anew by the action of the rays of radium.

The salts of radium are spontaneously luminous. It might be said that they make themselves luminous by the action of the Becquerel rays they emit. Anhydrous chloride and bromide of radium are the salts that give the most intense luminescence. They may be obtained so luminous that the light can be seen in full daylight. The light emitted by the salts of radium recalls in tint that from a fire-fly. The luminosity of the radium salt decreases with time without ever completely disappearing, and those that were colorless at first become gray, yellow or violet.

Physiological Effects of the Radium Rays.—The rays from radium cause different physiological actions.

A salt of radium placed in an opaque box made of cardboard or metal acts on the eye and produces the sensation of light. To obtain this result, the box containing the radium is placed before the closed eye or against the temple. In this experiment the center of the eye becomes luminous by phosphorescence under the influence of the radium rays, and the light one sees has its source in the eye itself.

The rays of radium act on the epidermis. If we place on the skin for a few minutes a bulb containing radium no particular sensation is felt. But fifteen or twenty days afterward it produces a reddening of the skin, then a slough in the place where the bulb was applied. If the action of the rays be long enough there is finally formed a sore that takes several

months to heal. The action of the rays from radium is analogous to that produced by the Roentgen rays. The attempt has been made to utilize this action in the treatment of lupus and cancer.

The radium rays also act upon the nervous centers and cause paralysis and death. (Danysz.) They seem also to act with especial intensity upon growing tissues. (Bohn.)

The Employment of Radium in the Study of Atmospheric Electricity.—The radium rays have also been utilized in the study of atmospheric electricity (Paulsen, Witkowski, Moureaux). A small quantity of a salt of radium placed at the extremity of a metallic rod serves as a point of contact for the potential. By this very simple arrangement we can avoid the use of flames or of water-dropping apparatus to measure the potential at any point in the atmosphere.

III. The Heat Given Off by the Salts of Radium.

The salts of radium continually give off heat. Its amount is sufficient for it to be detected by means of a crude experiment with two ordinary mercury thermometers. Two identical heat-insulating vacuum-bulbs are used. In one of these is placed a glass bottle containing 0.7 gram of pure radium bromide; in the second is placed a glass bottle containing some inactive substance, such as barium chloride. The temperature of the contents of each is shown by a thermometer placed with its bulb near the bottle. The mouths of the flasks are closed with cotton. Under these conditions the thermometer in the same flask as the radium always has a temperature 3° higher than that indicated by the other thermometer.

The quantity of heat given off can be estimated by means of a Bunsen ice calorimeter. By placing in the calorimeter a glass bottle containing a salt of radium, it is found that there is a continued supply of heat that stops as soon as the radium is removed. A determination made with a salt of radium that had been prepared a long time before shows that each gram of radium gives off 80 small calories an hour. Hence radium gives off enough heat to melt its own weight of ice every hour. Nevertheless the radium salt seems to re-

main in the same condition, and besides, not a single ordinary chemical reaction can be called in to explain such a continuous liberation of heat.

It has been shown, also, that a recently prepared salt of radium sets free a relatively small amount of heat. The heat set free in a given time then increases continually, and tends towards a definite value which is not quite reached at the end of a month.

When a salt of radium is dissolved in water and the solution enclosed in a sealed tube, the amount of heat given off at first is slight. It then increases and tends to become constant at the end of a month. When the limit is reached, the amount of heat given off from the radium in solution is the same as if it were in the solid state.

The amount of heat set free by radium at different temperatures can also be estimated by causing it to boil a liquefied gas and measuring the volume of gas that is liberated. The experiment can be performed with methyl chloride, which boils at —21°.

The experiment was also performed by Dewar and myself with liquid oxygen (—180°) and liquid hydrogen (—252°). The latter is especially suitable for the experiment. A tube, A, closed at the lower end and surrounded by a Dewar vacuum-bulb, contains a little liquid hydrogen, H. A delivery-tube, *tt*, allows the gas to be collected in a graduated tube filled with water. The tube, A, and its insulator are plunged into a bath of liquid hydrogen, H′. Under these conditions no gas is produced in the tube A. When a bottle containing 0.7 gram of radium bromide is placed in the hydrogen in A, there is a continuous liberation of hydrogen gas, and 73 cc. of the gas are collected per minute. (The radium bromide had been made only ten days before.)

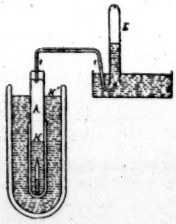


Fig. 1.

IV. Induced Radioactivity and Radioactive Emanations.

Induced Radioactivity.—Radium, thorium, and actinium

have the property of acting externally, apart from the Becquerel rays that they emit. They communicate little by little their radioactive properties to substances in their neighborhood, and the latter emit in turn Becquerel rays. The activity can be transmitted to gases, liquids, and solids. The phenomenon is known as induced radioactivity.

Induced radioactivity propagates itself in gases step by step by a sort of conduction, and is not at all due to direct radiation from the body which causes it.

When the activated substance is removed from the radioactive body, the induced radioactivity on it persists for a certain time. It diminishes, nevertheless, little by little and finally disappears.

Emanation.—To explain these phenomena, Rutherford supposes that radium and thorium are constantly giving off an unstable, radioactive, gaseous material, which he calls an emanation. The emanation spreads into the gas surrounding the radioactive substance. It destroys itself little by little by giving off Becquerel rays and by producing other unstable radioactive substances that are not volatile. These new substances attach themselves to the surface of solid bodies and render them radioactive.

Without stating so many hypotheses, we may adopt the name emanation to designate the radioactive energy in the form which it has when it spreads into the gas surrounding the radioactive substance. It may be supposed also, that this energy disappears in creating the energy of induced radioactivity in solids.

The Radioactivity Induced by Radium and the Emanation from Radium.—When a solid salt of radium is placed in a closed space filled with air, the interior walls of the closed space and all solids in it become radioactive. We may, for example, place inside the space a plate of any solid, leave it there a certain time, and then remove it to study its activity. It is found that the activity of the plate increases at first according to the length of its stay in the space, but that it reaches a limiting value after a sufficiently long time. When the ex-

cited plate is removed from the space it loses its activity according to an exponential law, the radiation falling to one-half its value in about half an hour. In a general way all solid substances under the same conditions acquire and lose their activity in the same manner.

The phenomena are much more intense (about twenty times), if instead of the solid salt of radium, we place a solution of it inside the closed space in an open vessel.

The nature and the pressure of the gas contained in the closed space have no influence upon the observed phenomena.

The induced activity in a closed space is proportional to the quantity of radium present.

When the space containing the radium communicates with a second by a tube, solids contained in the second become equally active after a sufficient time. The transmission of the activating property can even take place from one to the other through a capillary tube.

When the gas which has been made active by remaining in one space containing radium is passed into another, it retains for a considerable time the property of rendering radioactive solids that are brought in contact with it. The gas thus removed from the action of the radium gradually loses, nevertheless, its power of causing radioactivity. It disappears as a function of the time, according to an exponential law. It loses one-half of its value every four days.

To interpret this phenomenon it must be assumed that radium continuously gives off a constant radioactive emanation. This emanation spreads into the air in a closed space, and acting on solids, makes them radioactive. When the air is transferred to another space, the emanation is carried along with it. Finally, it is destroyed spontaneously with such velocity that the quantity of emanation in the gas diminishes by one-half every four days.

In a space containing radium there is established a state of equilibrium when the quantity of emanation in the space is such that the loss of emanation resulting from its spontaneous destruction is exactly compensated by the continued supply coming from the radium.

The following experiment can be performed: The glass receiver, A (Fig. II.), filled with air, communicates through the constricted part, O, with the bulb, B, which contains radium, S. At the end of a certain time the emanation has spread into A, and its interior walls have become active. The receiver, A, is then separated from the radium by closing O with a flame. The external radiation of A may then be studied by placing it in the interior cylinder of a cylindrical condenser (Fig. III.). The interior cylinder is of aluminium, BBBB. It is brought to a potential of 500 volts. The external cylinder, CCCC, of the condenser is of copper. It is in connection with an electrometer and piezoelectric quartz. By means of the quartz the current passing through the condenser is measured. This current is caused by the Becquerel rays that escape from the tube A, pass through the cylinder of aluminium B, and make the air between the two cylinders a conductor of electricity. The apparatus is surrounded by a protective metallic envelope, EEEE, connected with the earth.

Fig. II.

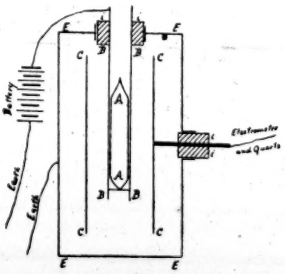


Fig. III.

It is found that the radiation from the tube A diminishes with time according to an exact exponential law, expressed by the equation

$$I = I_0 e^{-at}.$$

I_0 is the value of the radiation at the beginning of the time, I the value at the instant t, and a a constant coefficient. $a = 2.01 \times 10^{-6}$, taking one second as the unit of time. The radiation falls to one-half its value after about four days.

In a second experiment the tube A may be made active as before, and the interior can then be evacuated by pumping out the air containing the emanation. Under these conditions the radiation of the receiver, A, diminishes much more rapidly, and becomes twice as feeble in about half an hour. This law of loss of activity is the same as that according to which excited bodies lose their activity when they are exposed to the free air. The result is the same if inactive air be admitted to the receiver, A, after having been evacuated.

One is thus led to the conclusion that in the first experiment the activity of the receiver, A, is caused by the air charged with the emanation contained in the receiver, and that the law of the diminution of the radiation in this experiment represents as well the law of the spontaneous disappearance of the emanation.

When a vacuum is produced in the receiver, A, which contains air charged with the emanation, and when the radiation of the receiver is measured immediately after the extraction of the air, it is found that the radiation has not changed at the moment when the active air is withdrawn. The Becquerel radiation of air charged with the emanation does not, then, produce any action in this experiment. This radiation probably exists, but it is composed of very slightly penetrating rays, incapable of passing through the glass wall. In this connection the following experiment can be performed. One of the ends of the metallic tube, AAAA (Fig. IV.), communicates at O by means of a rubber tube with a receiver, B, in which is a solution of a radium salt. The other end of the tube, A, is closed with an insulating stopper, i. Through the stopper passes a metallic rod, C, connected with an electrometer. The tube, A, and the rod, C, form a cylindrical condenser. The tube, A, is brought to a potential of 500 volts. The metallic tube, DDDD, connected with the earth, serves as a guard-tube. When the tube, A, is sufficiently

active it is removed from the radium, and the intensity of the

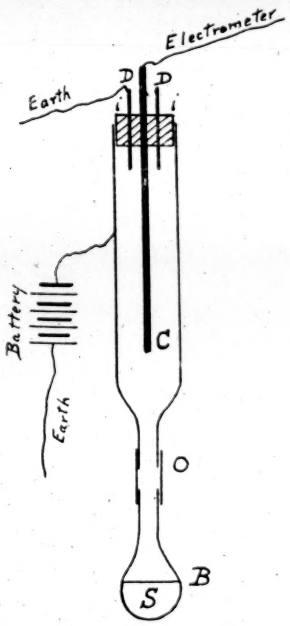


Fig. IV.

current passing through the condenser is measured. Then the active air which fills the condenser is rapidly driven out, inactive air is admitted, and a new measurement of the intensity of the current is made immediately. It is found that the current has become six times more feeble. Thus, during the second measurement the radiation of the excited walls acts solely to ionize the air in the condenser, while during the first measurement the emanation acts as well. We may, then, suppose that it also emits an emanation. This radiation is

necessarily very slightly penetrating, for its action cannot be detected on the exterior.

When a solid plate which has been excited by the emanation becomes inactive in free air, the law of loss of activity depends on the time during which the plate has been left in contact with the emanation. If the action of the emanation is prolonged (more than twenty-four hours, for example), the law of loss of activity is given by the difference between two exponentials. The intensity of the radiation, I, may in this case be represented as a function of the time, t, by the equation

$$I = I_0[Ke^{-bt} - (K-1)e^{ct}].$$

I_0 is the intensity of the radiation at the beginning of the time, that is at the moment when the plate is removed from the influence of the emanation. K, b, and c are three constant coefficients: $K = 4.2$; $b = 0.000413$; $c = 0.000538$, taking one second as the unit of time.

These results are represented by the curve 1 (Fig. V.). The logarithm of I is represented on axis of the ordinates, and the time on the axis of abscissas. One hour and a half after the beginning of the loss of activity the second exponential has become negligible with respect to the first in the expression for the value of I, and the representative curve has become straight. From this moment the activity diminishes by one-half during each period of twenty-eight minutes.

If the duration of the action of the emanation is not so long, the law of the variation of the radiation during its loss is much more complex. In Fig. V. are represented the results of experiments for different times of action, as indicated on the corresponding curves. We see, for example, that for a time of excitation of five minutes, the intensity of the radiation during the loss of activity first falls rapidly to a minimum; then it increases, and again begins to fall. Finally, the law of loss of activity tends towards a simple exponential law which is the same as the limiting law after prolonged excitation. These complex phenomena can be explained by assuming that on the excited plate the radioactive energy is in three distinct states, but the demonstrations relative to this subject are too long to have a place in this article.

The emanation from radium causes the energetic phosphor-

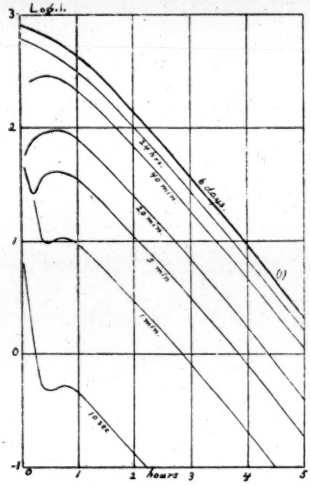


Fig. V.

escence of a large number of substances. Glass reservoirs containing air charged with the emanation are luminous, Thuringian glass being the most sensitive. Phosphorescen sulphide of zinc is particularly sensitive to the action of the emanation from radium, and then gives an intense light.

If in a closed space substances become more active the greater the amount of free gas around them. When plates placed parallel to one another, and a short distance apart, are put into a closed space with radium, the faces of each plate become excited in proportion to its distance from the others. When glass tubes of different diameters are filled with the emanation and communicate with one another, the walls of those of greatest interior diameter become most active. These tubes are also most luminous. To interpret these facts it must be assumed that the air charged with the emanation acts

on the walls by a radiation that arises in every part of the gaseous mass, and that the radioactivity induced upon a wall is proportional to the flow of exciting radiation received by that wall.

The Slow Evolution of Induced Activity.—A solid body acquires a very feeble, persistent, induced activity when it remains a month or less in contact with the radiation from radium. A substance withdrawn from the influence of the emanation after having been subjected to it for a long time loses its activity rapidly at first, according to the laws given. But the activity of the radiation does not disappear completely. There remains a radiation several thousand times more feeble than it was at first. This radiation is given off with extreme slowness and continues for several years. (The radiation passes through a minimum, then slowly increases for several months, but always remains very slight.)

Occlusion of the Emanation of Radium by Solids.—All solids when excited by contact with the emanation from radium acquire the property of themselves emitting the emanation in very small quantity. They preserve this power for only twenty minutes from the time they are removed from the space containing the emanation. Nevertheless certain substances as caoutchouc, paraffin, and celluloid have the property of being saturated with the emanation, and of emitting it afterwards in abundance for several hours, or even days.

Induced Activity of Liquids.—When a liquid is placed in a closed space with radium it becomes radioactive. Water, salt solutions, petroleum, etc., can thus be excited. The liquids dissolve a certain amount of the emanation. When an excited liquid is separated from the radium and sealed up in a tube it slowly loses its activity according to the law of the destruction of the emanation (decrease to one-half in four days). When the liquid is placed in a flask open to the air it loses its activity very rapidly, and the emanation spreads into the surrounding air.

Variations of the Activity of Solutions of Radium Salts and of the Solid Salts of Radium.—When a solution of a salt of radium

is exposed to the air of a room in an open vessel it becomes almost inactive. The solution emits an emanation that spreads into the room and causes induced radioactivity of the walls. The radiation of the radium is thus externalized. If the solution be enclosed in a sealed tube its activity increases little by little, and tends toward a limiting value that is reached only after several months. No doubt the emanation produced by the radium accumulates in the tube until the velocity of its spontaneous destruction is equalized by the supply from the radium.

We have seen that a salt of radium that has been freshly prepared possesses an activity which increases with the time, and becomes about five times as great as the initial activity. It seems that the emanation emitted by the radium can escape only with difficulty from the solid salt, and that it accumulates there and is transformed at once into induced radiation. An equilibrium is established when the spontaneous loss becomes sufficient to compensate the production.

When solid salt of radium is heated to redness, all the emanation which it had accumulated escapes. When the salt returns to the temperature of the room it emits Becquerel rays to a much less extent. However, the radiation recovers little by little its original value, which is reached after one or two months. The salt which had been heated to redness no longer possesses the power of emitting the emanation, but this property may be restored to it by dissolving it and drying it at a slightly elevated temperature.

Diffusion of the Emanation from Radium.—Danne and I have studied the law of the diffusion of the emanation of radium. A large glass reservoir filled with excited air communicates with the atmosphere by means of a capillary tube. The Becquerel radiation emitted by the walls of the reservoir is measured as a function of the time, and from this is deduced the law of the escape of the emanation through the capillary tube. It is found that the rapidity of the escape of the emanation is proportional to the quantity of it in the reservoir. It varies proportionally to the cross section of the capillary tube, and inversely as its length. These laws are the

same as for a gas mixed with air under the same conditions. The coefficient of the diffusion of the emanation into air is equal to 0.100 at 10°. The coefficient is, therefore, of the same order of magnitude as that of the diffusion of carbon dioxide into the air, which is equal to 0.15 at the same temperature.

Radioactivity Induced by Thorium and the Emanation of Thorium.—Thorium emits an emanation and gives rise to the phenomena of induced radioactivity. These properties have been made the subject of numerous researches by Rutherford. The action of thorium is, otherwise, considerably less intense than that of radium.

The emanation of thorium disappears spontaneously according to a simple exponential law, but its disappearance is much more rapid than that of the emanation of radium. The quantity of the emanation from thorium diminishes by one-half in about one minute and ten seconds, while in the case of radium the quantity falls to one-half in four days. This considerable difference causes a profound difference in the aspect of the phenomena.

In a closed space of not too great dimensions the emanation from radium spreads almost uniformly into all parts. But under the same conditions the emanation of thorium is found to accumulate in the vicinity of the thorium, because it disappears spontaneously before it has time to diffuse any considerable distance into the air.

The radiant activity of a substance can be measured by placing it upon the lower plate of a condenser formed of two horizontal plates, and measuring the conductivity communicated to the air between the plates. If this measurement be made with oxide of thorium, it is found that the conductivity of the air is greatly decreased when a current of air is sent between the plates. The oxide of thorium emits, indeed, an emanation that accumulates upon the substance and by its radiation helps to ionize the air between the plates. A current of air carries away the emanation as rapidly as it is set free, and the only thing left to cause ionization is the Becquerel radiation coming directly from the thorium.

If the same experiment be repeated with a salt of radium it is found that the current of air produces only a feeble effect. With uranium and polonium, which do not emit the emanation, the current of air has no effect. On the contrary, in the case of actinium, the action of the current of air is to suppress four-fifths of the conductivity of the air. It may be concluded that for thorium, and especially for actinium, the radiation of the emanation is very important in comparison with the radiation of the radioactive substance itself.

When one wishes to excite a solid to saturation with the emanation from thorium, it is necessary to cause the emanation to act for a long time, and hence new supplies of it must be brought continually to the surface of the body that is to be excited. To do this a current of air is passed through a solution of a salt of thorium and, then this current, of air charged with the emanation, is passed over the body. The solid, when excited by the emanation from thorium, loses its activity spontaneously according to an exponential law. The radiation falls to one-half every eleven hours. Hence, contrary to what takes place with the emanations, the activity induced by thorium upon solid substances disappears more slowly than that induced by radium.

Radioactivity Induced by Actinium and the Emanation from Actinium.—Actinium emits an emanation which gives a very intense radiation. This emanation disappears spontaneously with extreme rapidity, and diminishes by one-half in about one second. In air at the atmospheric pressure the emanation emitted by actinium cannot propagate itself to a greater distance than 7 or 8 mm. from the active substance, and excites bodies only when they are placed very near the source. On the contrary, in a vacuum the diffusion is rapid, and a body placed 10 cm. away from the actinium can be excited. The radioactivity induced by the actinium upon solids disappears according to an exponential law. It diminishes to one-half in about thirty-six minutes.

The Concentration of Induced Radioactivity upon Bodies Charged Negatively.—Rutherford showed that a body exposed to the emanation from thorium became much more active

when it was charged negatively than when it was at the same potential as the surrounding objects. On the contrary, it became less excited when it had a positive potential. The same phenomenon is noticed in the case of the excitation by radium and actinium. The nature of this curious phenomenon seems to me not to be well established.

Condensation of the Emanations from Radium and Thorium.—Rutherford and Soddy discovered that the emanations from radium and thorium can be condensed at the temperature of liquid air. A current of air charged with the emanation loses its radioactive properties when passing through a coil of tube plunged in liquid air. The emanations remain condensed in the tube, and can be restored to the gaseous state when it is warmed. The emanation from radium condenses at —150°, while that from thorium condenses between —100° and —150°. The experiment can be performed as follows: Two glass reservoirs, one large and the other small, communicate with one another. They are filled with gas excited by radium. The small reservoir is plunged in liquid air. The large reservoir then rapidly becomes inactive, while all the activity is concentrated in the small reservoir. If the two are then disconnected, and the small one be taken from the liquid air, it is seen that the large reservoir is not at all luminous, while the small one gives off more light than at the beginning of the experiment. The experiment is a very brilliant one if the walls of the reservoirs are coated inside with phosphorescent sulphide of zinc.

When a platinum wire excited by thorium or radium is heated to redness, it loses most of its activity. Fanny Cook Gates showed that this radioactivity is transferred to cold solids placed in the vicinity of the wire. It distils in some way, at a sufficiently high temperature, passing through the intermediate form of a gaseous emanation. The induced radioactivity of solids would thus be analogous to a condensed emanation.

Activity Induced by Remaining in Solution in a Radioactive Liquid. Uranium X. Thorium X.—Certain substances are temporarily excited when they stay in the same solution with

radioactive substances. Giesel and Mme. Curie prepared active bismuth by dissolving one of its salts in the solution of a salt of radium. Debierne also excited a salt of barium in a solution of a salt of actinium. The barium salt thus excited presents certain analogies to the salt of radium, and can be fractionated in the same way. By crystallization the active chloride is concentrated in the salt that is deposited.

By various methods of chemical precipitation the activity of uranium has been divided (Crookes, Soddy, Rutherford and Grier, Debierne, Becquerel). For instance, barium chloride is added to a solution of uranyl nitrate, and the barium is then precipitated by adding a little sulphuric acid. The precipitated barium sulphate, when separated and dried, is radioactive. It has carried with it a part of the activity of the uranium, for the uranium salt, when the solution is evaporated to dryness, is less active than before it was submitted to this operation. But after several months the sulphate of barium loses its radioactivity, while the uranium salt has regained its original properties. It is evident that the barium was excited by contact with the uranium, or that it occluded in some special form a part of the activity of the uranium (uranium X of Crookes).

Rutherford and Soddy showed that if nitrate of thorium is precipitated by ammonia, the precipitated oxide of thorium is less active than ordinary thorium. The liquid from which it was precipitated is radioactive, and on evaporating it to dryness the small residue is 2,500 times more active than the thoria (they call the radioactive substance in this residue thorium X). After several weeks the residue has lost its activity, the thorium X has disappeared, and the thoria which was precipitated has, on the contrary, regained its normal activity. Further, while the thorium X existed it emitted the thorium emanation in abundance.

Rutherford and Soddy think that uranium X and thorium X are simply intermediate products of the breaking down of uranium and thorium. Thorium, for example, produces thorium X continuously, which breaks down into the emanation of thorium, that is in its turn transformed into induced activity.

Conductivity of Atmospheric Air. Emanation and Induced Radioactivity at the Surface of the Earth.—Elster and Geitel, and also Wilson, showed that atmospheric air conducts electricity to a slight extent, that it is always slightly ionized. This ionization seems to be due to various causes. According to the work of Elster and Geitel, atmospheric air always contains a small proportion of an emanation analogous to that emitted by radioactive substances. Metallic wires suspended in the air and kept at a high negative potential become active under the influence of this emanation. At the summits of high mountains the atmosphere contains more of the emanation than on plains or at the level of the sea. The air of caves and caverns is especially highly charged with the emanation. Air rich in the emanation can also be obtained by aspirating, by means of a tube sunk in the earth the air which is contained in it. The air extracted from certain mineral waters contains the emanation, while the air dissolved in the water of the sea and of the rivers is almost free from it.

The conductivity of the atmosphere is also probably due in part to very penetrating radiations that traverse space, and of which the origin is unknown. Finally, it is probable that all bodies are slightly radioactive, and that those at the surface of the ground render the air around them a conductor of electricity.

Time-Constants that Characterize the Disappearance of Emanations and of Induced Radioactivity.—We have seen that the radioactive emanations and the induced radioactivity of solids disappear spontaneously, and that the law of their disappearance is, in general, a simple exponential law. The intensity of the radiation, I, is given as a function of the time, t, by the formula,

$$I = I_0 e^{-at}.$$

I_0 is the intensity of the initial radiation, and a a constant. This exponential law is completely defined by the knowledge of a constant of time that may be, for example, the inverse of a in the preceding formula. One may also take as the con-

stant the time necessary for the intensity of the radiation to diminish to one-half.

It is very remarkable that these constants of time seem to be invariable under widely different circumstances. Thus it is that the emanation from radium diminishes to one-half during each period of four hours, whatever may be the conditions of the experiment, and whatever the temperature between —180° and +450°. The rate of its disappearance is the same whether the emanation be in the gaseous state (room temperature) or condensed (—180°). The properties of the emanation from radium thus give us an invariable standard of time which is independent of all agreements as to the unit.

The time-constants of the radioactivity serve to characterize in a precise manner the nature of the different radioactive energies.

The following are the times necessary for the activity to fall to one-half of its value :

	Time.
Emanation of	
Radium	4 days
Thorium	1 minute 10 seconds
Actinium	Several seconds
Induced radioactivity of	
Radium	1 hour (after beginning of the loss. 28 minutes (for times more than two hours after the beginning of the loss)
Thorium	11 hours
Actinium	36 minutes

Thus J. J. Thomson and Adam found recently that the emanation from water from certain sources falls to one-half for each period of four days, and that this emanation causes induced activity in solids which falls to one-half in about forty minutes. The supposition is that the emanation contained in the water is due to radium.

Ordinary thorium extracted from monazite sand is slightly radioactive. Thorium from pitchblende is strongly radioactive (thorium with actinium of Debierne). The radioactivity

in the two cases is not due to the same substance, for the time-constants of the emanation and of the radioactivity are different.

Certain radioactive substances like actinium have never been separated in a pure state, and it may be supposed that the very active substances that have been studied contain only traces of them. The chemical reactions of substances cannot be recognized with certainty when they are found solely in a diluted condition, mixed with other substances. Under those circumstances one element may carry another down with it in a precipitation, and the action of the reagent is not the same as when we have pure compounds. Hence the chemical reactions will not serve to characterize a radioactive substance. It may, however, be recognized under all circumstances by the time constants of the emanation it emits, and of the induced radioactivity excited by that emanation upon solids.

Nature of the Emanation.—According to Rutherford, the emanation of a radioactive substance is a radioactive, material gas which escapes from it. In fact, the emanation from radium acts in many ways like a gas.

When we put in communication two glass reservoirs, one containing the emanation and the other none, the emanation diffuses into the second and, when equilibrium is established, it is found that the emanation is divided between the two reservoirs according to their respective volumes. One of the two may be heated to 350°, while the other remains at the room temperature, and it is found that in this case, also, the emanation is divided between the two reservoirs as if it were a perfect gas obeying the laws of Marriotte and Gay-Lussac.

We have also seen that the emanation from radium diffuses into the air according to the law of the diffusion of gases, and with a coefficient of diffusion comparable with that of carbon dioxide. Finally, the emanations from radium and thorium condense at low temperatures like liquefiable gases.

At the same time it should be remembered that no one has yet observed any pressure due to the emanation, nor has any one shown by weighing that a material gas is present. All

our knowledge of the properties of the emanation results from measurements of radioactivity. More than that, no one has yet shown with certitude that there is a characteristic spectrum produced by the emanation.

The emanation should also not be considered as an ordinary material gas, for it disappears spontaneously from a sealed tube containing it, and the rapidity of its disappearance is absolutely independent of the conditions of the experiment, especially of the temperature.

It is very curious that the numerous attempts made under the most varied conditions to obtain chemical reactions with the emanation have been fruitless. To explain this fact Rutherford thinks that the emanations are gases of the argon family.

The following facts are difficult to explain. The emanation from radium condenses at —150°, and according to Rutherford, a current of air at —153° may be passed over it continuously without removing it. The amount of the emanation must be very small, and if it had the slightest tension at —153°, it would quickly evaporate in a current of air. Further, the temperature of condensation by cooling should be a function of the amount of the emanation in a given volume of air, which has not yet been proved.

Debierne and I have found that the emanation passes with extreme ease through the tiniest holes and fissures in solids, while under the same conditions the ordinary gases could circulate only with the greatest slowness.

Rutherford supposes that radium destroys itself spontaneously, and that the emanation is one of the products of the breaking-down. Debierne and I observed that a solid salt of radium quite rapidly excites the walls of the reservoir filled with air, which contains it, by the emanation which it emits. On the contrary, if a quite perfect vacuum be made in the reservoir the excitation takes place only with extreme slowness; but it rapidly reappears when a gas has been admitted. However, the emanation spreads much more rapidly in a gas at very low pressure than at the atmospheric pressure. It seems from this that the emanation experiences some par-

ticular difficulty in escaping from radium which is in a vacuum.

Disengagement of Gas by the Salts of Radium. Production of Helium.—Giesel noticed that solutions of radium bromide continually give off gases. These gases are principally hydrogen and oxygen, in the same relative proportion as in water, and might, therefore, come from the decomposition of the water of the solution. But Ramsay and Soddy also showed that there always is a small quantity of helium that they detected by its spectrum in a Geissler tube. The helium lines were also accompanied by three unknown lines.

A solid salt of radium also constantly gives off gases capable of producing a pressure in a closed tube. To this liberation of gas can be attributed two accidents during my experiments. A sealed bulb of thin glass, almost filled with well-dried bromide of radium, exploded and became slightly warm at the same time. An explosion was also caused by dry radium chloride when heated quite rapidly in a vacuum to 300°. In this case the explosion seemed to be caused by fragments of the solid salt filled with occluded gas.

At the moment we dissolve in water a solid salt of radium that has been prepared a long time, there is an abundant evolution of gas.

The spontaneous production of helium in a sealed tube containing radium is plainly a new fact of fundamental importance. Ramsay and Soddy accumulated some of the emanation from radium, and enclosed it in a Geissler tube at low pressure. They obtained new lines which they attributed to the emanation, and they also showed that the spectrum of helium was absent at first, but that it came into being little by little in the tube. According to that, helium must be one of the products of the disintegration of radium.

In support of the preceding results may be mentioned some points noticed by Mme. Curie and me at the beginning of our work. We were struck by the simultaneous occurrence of uranium, radium, and helium in the same mineral. We took 50 kilograms of commercial barium chloride, coming from minerals that did not contain uranium, and submitted it to

fractional crystallization to see whether it contained traces of radium chloride. After a prolonged fractionation, the portion at the head, now reduced to a few grams, was not at all radioactive. Hence, barium contains radium only when it comes from uranium minerals. These are the same that contain helium. One might think that there is a relation of cause and effect from the simultaneous occurrence of these three substances.

This rapid summary of the researches on radioactivity serves to show the importance of the scientific movement that has been started by the study of this phenomenon. The results obtained are of a nature to modify the ideas one might have about the invariability of the atom, the conservation of matter and of energy, the nature of the mass of bodies, and the energy spread through space. The most fundamental questions of science are thus brought into the discussion. Apart from the theoretical interest of which they are the object, the phenomena of radioactivity give new means of action to the physicist, the chemist, the physiologist, and the physician.

BIBLIOGRAPHY.

Radiation from Uranium.—Becquerel: Compt. rend., 1896–7, different notes; Mme. Curie: *Ibid.*, April, 1898; Rutherford: Phil. Mag., 47, 109 (1899).

Radioactive Minerals.—Mme. Curie: Compt. rend., April, 1898.

Radiation of Thorium.—Schmidt: Wied. Ann., 65, 141; Mme. Curie: Compt. rend., April, 1898; Rutherford: Phil. Mag., 47, 109 (1899); Owens: *Ibid.*, Oct., 1899.

Radiation of Polonium.—P. Curie and Mme. Curie: Compt. rend., July 18, 1898; Mme. Curie: Rev. Gen. des Sciences, Jan. 30, 1899; Mme. Curie: Compt. rend., Jan. 8, 1900. Thèse de doctorat, June, 1903; Becquerel; Compt. rend., 129, 1230; 130, 979, 1154; Marckwald: Ber. d. chem. Ges., June and Dec., 1902; Becquerel; Compt. rend., April 27, 1903 (α-rays), and Feb. 16, 1903.

Radium.—P. Curie, Mme. Curie and Bémont: Compt. rend., Dec. 26, 1898.

Atomic Weight of Radium.—Mme. Curie: Compt. rend., Nov. 13, 1899, Aug., 1900, July 21, 1902; Thèse de doctorat, 1903; Phys. Ztschr., 1903, p. 456.

Spectrum of Radium.—Demarcay: Compt. rend., Dec., 1898, Nov

1899, July, 1900; Giesel: Phys. Ztschr., Sept. 15, 1902; Runge and Precht: *Ibid.*, 4, 285 (1903).

Radiation of Radium.—M. and Mme. Curie: Compt. rend., Nov., 1899, Jan. 8, 1900, pp. 73 and 76, March 5, 1900 (electric charge of the rays), Feb. 17, 1902 (conductivity of liquids under the influence of the rays); Becquerel: *Ibid.*, Dec. 4, 11, and 26, 1899, Jan. 29, Feb. 12, April 9 and 30, 1900; Giesel: Wied. Ann., 69, 91, 834; S. Meyer and V. Schweidler: Acad. de Vienne, Nov. 3 and 9, Dec. 7, 1899; Kaufmann: Nachrichten der K. Ges. Wiss. Göttingen, 1901, Heft 2; Rutherford: Phil. Mag., 4, 1 (1902).

α-Rays of Radium.—Rutherford: Phil. Mag., Feb. 1903; Becquerel: Compt. rend., Jan. 26, Feb. 16, June, 1903; Des Coudres: Phys. Ztschr., June 1, 1903; Crookes: (spinthariscope) Chem. News, April 3, 1903.

Heat Given Off by Radium.—P. Curie and Laborde: Compt. rend., March 16, 1903; P. Curie: Roy. Inst. June 19, 1903.

Actinium.—Debierne: Compt. rend., Oct. 16, 1899, April 2, July 30, 1900; Feb. 16 and March 16, 1903.

Radioactive Lead.—Giesel: Ber. d. chem. Ges., 34, 3779 (1901); Hofmann and Strauss: *Ibid.*, 33, 3126 (1900).

Radioactivity of all Substances.—Strutt: Phil. Trans., 1901; Phil. Mag., June, 1903; MacLennan and Burton: *Ibid.*, June, 1903; Lester Cooke: *Ibid.*, October, 1903.

Induced Radioactivity and the Emanation of Radium.—P. Curie and M. Curie: Compt. rend., Nov. 6, 1899; P. Curie and Debierne: *Ibid.*, 1901 (5 notes); P. Curie: *Ibid.*, Nov. 17, 1902, Jan. 26, 1903; P. Curie and J. Danne: *Ibid.*, Feb. 9 and June 2, 1903: Dorn: Abhand. Naturforsch. Ges. Halle, June, 1900: Rutherford: Phys. Ztschr., April 20, 1901, Feb. 15, 1902; Rutherford and Miss Brooks: Chem. News, April 25, 1902; Rutherford and Soddy: J. Chem. Soc. (London), April, 1902; Rutherford: Phys. Ztschr., March 15, 1902, Phil. Mag., Nov., 1902, Jan., 1903; Rutherford and Soddy: (condensation of the emanations) J. Chem. Soc. (London), Nov. 19, 1902. Phil. Mag., May, 1903.

Induced Radioactivity and the Emanation of Thorium.—Rutherford: Phil. Mag., Jan. and Feb., 1900; Phys. Ztschr., April 20, 1901; Rutherford and Soddy: J. Chem. Soc. (London), April, 1902; Phil. Mag., 1902, pp. 370, 569; Rutherford: Phys. Ztschr., Feb. 15, March 15, 1902, Phil. Mag., Nov., 1902, Jan., 1903.

Radioactivity and Ionization of the Atmosphere and of Spring Water.—Elster and Geitel: Phys. Ztschr., 1900, 1901; Wilson: Proc. Roy. Soc. (London), 1901; Rutherford and Allen: Phil. Mag., Dec. 24, 1902; Elster and Geitel: Phys. Ztschr., Sept. 15, 1902; MacLennan: Phil. Mag., 5, 419; MacLennan and Burton: *Ibid*, June, 1903; Saake: Phys. Ztschr., 1903; Lester Cooke: Phil. Mag., Oct., 1903; J. J. Thomson: Conduction of Electricity through Gases, Cambridge, 1903.

Gases Given Off by Radium.—Giesel : Ber. d. chem. Ges., **36**, 347 (1903) ; Ramsay and Soddy : Phys. Ztschr., Sept. 15, 1903.

Physiological Effects of the Becquerel Rays. Action on the Epidermis. Walkhoff : Phot. Rundschau, Oct., 1900 ; Giesel : Ber. d. chem. Ges., **33** ; Becquerel and Curie : Compt. rend., **132**, 1289. *Action on the Eye.* Giesel : Naturforscherversammlung, 1899 ; Himstedt and Nagel : Ann. Phys., **4**, 1901.

Physiological Action.—Aschkinas and Caspari : Ann. Phys., **6**, 570 (1901) ; Danysz : Compt. rend., Feb. 16, 1903 ; Bohn : *Ibid.*, April 27 and May 4, 1903. *Treatment of Lupus.*—Danlos : Soc. Dermatologie, Nov. 7, 1901 ; Hallopau and Gadaud : *Ibid.*, July 3, 1902 ; Blandamour : Thesis, Faculté de Médecine de Paris, 1902.

NOTE.

To the Editor, American Chemical Journal :

In the February number of the AMERICAN CHEMICAL JOURNAL appeared an article by Keiser and Forder, suggesting still another method for solving the long vexed problem of the determination of free lime in cements. Every cement chemist in the world would welcome with pleasure even an approximately accurate method which could always be depended upon for distinguishing between the lime which is combined with the silica, and that which remains free in cements. Up to the present time, there have been 53 researches, comprising 25 different methods of attack, published on this subject. (See Ztschr. angew. Chem., **20**, 466.). As a matter of fact, the problem remains to-day unsolved.

Keiser and Forder, after speaking of the objections to the use of water or watery solutions, as a method of attack, proceed to describe a method in which a small fraction of a gram of cement is wetted with water, then subsequently dried and weighed. Every cement chemist knows that on wetting cement the tri-calcic silicate is quickly broken down with an accompanying formation of calcic hydroxide. We are now told that if free lime is already present the reaction will not proceed in that direction, or at least not quickly enough to involve the basic silicates present. It seems difficult to believe, in the light of past investigation, that this is possible. It would almost seem that the authors were not aware that methods involving the use of absolute alcohol have been abandoned, as it has been shown that even alcohol breaks down tri-calcic silicate with the formation of free lime.

Jordis and Kantner have pointed out in a most comprehensive article (loc. cit.) the harm that has been done by the

attempt to draw important deductions from data yielded by similar analytical methods. Is history to repeat itself?

A. S. CUSHMAN.

ROAD MATERIAL LABORATORY, BUREAU OF CHEMISTRY,
WASHINGTON, D. C., Feb. 12, 1904.

REVIEWS.

PRAKTISCHE UEBUNGEN ZUR EINFÜHRUNG IN DIE CHEMIE. Von DR. ALEXANDER SMITH, Professor für Chemie an der Universität Chicago. Nach einer vom Verfasser besorgten Umarbeitung der zweiten amerikanischen Auflage ins Deutsche übertragen von PROFESSOR DR. F. HABER und DR. M. STÖCKER. Karlsruhe: G. Braun, 1904.

In the preface, Professor Haber gives at some length his reasons for making this translation. He refers to the fact that the teachers of chemistry in American universities and colleges have frequently studied in Germany, and says that while American teachers with one accord pursue German methods of instruction in advanced chemical work, probably not one of these teachers has copied the German method of instructing beginners in the laboratory, commencing with systematic qualitative analysis, and entirely omitting work on general chemistry. Professor Haber finds the American method of beginning laboratory work by study of general chemistry the better of the two, and wishes his countrymen to try it.

German and American laboratory usage differ in that the tendency here is perhaps to over-coddle the beginner, while in Germany, in the past at least, it has been to neglect him.

Dr. Haber does not seem to know that this is not the first book of the American school which has been translated into German. Seubert made a translation of Remsen's Introduction to the Study of Chemistry, which was published in Tubingen in 1887, and in Stuttgart in 1895. This book, *if used properly*, covers practically the same ground in laboratory work in general chemistry as Dr. Smith's book.

It is to be hoped that these translations of American methods may in time help the beginner in the German laboratory, as Dr. Haber wishes and hopes, but this hope will not be realized until the laboratory teacher and his assistants really give their best effort and their entire effort during the laboratory hours to instruction.

That Dr. Haber too realizes this is evident, for he says in the preface that this method requires the constant supervision of the teacher and assistants, of whom one should be alloted to ten or at most twenty students.

Professor Smith's book is not a text-book, but a laboratory manual and an excellent one. It differs in three essentials from most books covering the same ground. First, it begins by explaining quantitative use of balance and of measuring apparatus with application to simple physical laws, *i. e.*, specific gravity of liquids and solids, laws of Gay-Lussac and Boyle. Further quantitative experiments on combining weights, multiple proportions, molecular weights, etc., are scattered through the book. Second, under the heading "Ion reactions and reactions between acids, bases and salts," a few simple experiments illustrating the dissociation theory are introduced. Third, the book contains no equations and is full of questions, and demands that the student shall write the equations in his note-book and shall study text-books to find answers to questions.

These last excellent features, which compel the thought and attention of the student, were first systematically used twenty-five years ago by Professor Volhard, now of Halle, at that time of Munich, in his admirable notes on qualitative analysis, which are still in use in the Munich laboratory. Dr. Haber informs us that Dr. Smith received his chemical education in Munich; it is possible that study with Volhard led him to use this method in his manual, which now, if Dr. Haber's hopes are fulfilled, may supply an undoubted want in German laboratory instruction.

HYPOCHLORITE UND ELEKTRISCHE BLEICHE. TECHNISCH-KONSTRUKTIVER THEIL. Von VIKTOR ENGELHARDT, Oberingenieur und Chefchemiker der Siemens und Halske Aktien-Gesellschaft, Wien. Mit 266 Figuren und 64 Tabellen im Text. Halle a. S. Wilhem Knapp, 1903. Preis M. 12.

This book is the eighth volume of the "Monographien über angewandte Elektrochemie." The name of the author is a guarantee for thorough work. He treats the subject of electric bleaching in two volumes, of which the present is devoted to the technical and constructive side and to the patent literature; the second volume, which will be published later, is to include the practical application of various methods with reference to relative profit, the analysis of raw materials and products, and the theoretical side of the subject.

It follows that while the present volume contains little of interest to most chemists, it is of great interest to those engaged in the manufacture of "bleach." Ninety-three patented methods are described, the more important ones in great detail, with abundant illustrations. Of special interest are the tabulated summaries, giving descriptive data, com-

parative efficiency, and relative expenses of the different systems. E. R.

JAHRBUCH DER CHEMIE: Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig; C. A. BISCHOFF, Riga; M. DELBRÜCK, Berlin; O. DOELTZ, Clausthal; J. M. EDER, Wien; P. FRIEDLAENDER, Wien; C. HARUSSERMANN, Stuttgart; A. HERZFELD, Berlin; F. W. KÜSTER, Clausthal; W. KÜSTER, Tübingen; J. LEWKOWITSCH, London; A. MORGEN, Hohenheim; F. QUINCKE, Leverkusen; A. WERNER, Zürich. Herausgegeben von RICHARD MEYER, Braunschweig. XII, Jahrgang, 1902. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn, 1903.

This excellent and most acceptable report continues to fulfill the expectations of chemists, and it may now be regarded as indispensable. A few changes and additions have been made to the staff of co-workers. Professor A. Werner and Dr. Pfeiffer, of Zurich, have prepared the chapter on Inorganic Chemistry in place of Professor Muthmann. A special examination of this chapter shows, as was to be expected, that the work is well done. A new section in the inorganic chemical industries has been added. This has been prepared by Dr. F. Quincke, of Leverkusen. It is interesting to note that the contact process for the manufacture of sulphuric acid has led to attempts to devise a contact process for the manufacture of nitric acid by conducting a mixture of ammonia and atmospheric air over heated metals or metallic oxides. It is stated that the manufacture of nitric acid from the air by means of electric sparks cannot be carried out economically in Germany. But these are details. Almost every page is of interest to the working chemist. I. R.

JAHRBUCH DER CHEMIE: Heausgegeben von RICHARD MEYER, Braunschweig. General Register über die Jahrgänge 1891 bis 1900 (Bände 1 bis 10). Bearbeitet von W. WEICHELT, Korpsstabsapotheker, A. D., Coblenz. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn, 1903.

This index to the first ten volumes of the Jahrbuch seems to have been carefully prepared. Wherever the ten volumes are found there this index should be also. It covers 319 pages and is clearly printed.